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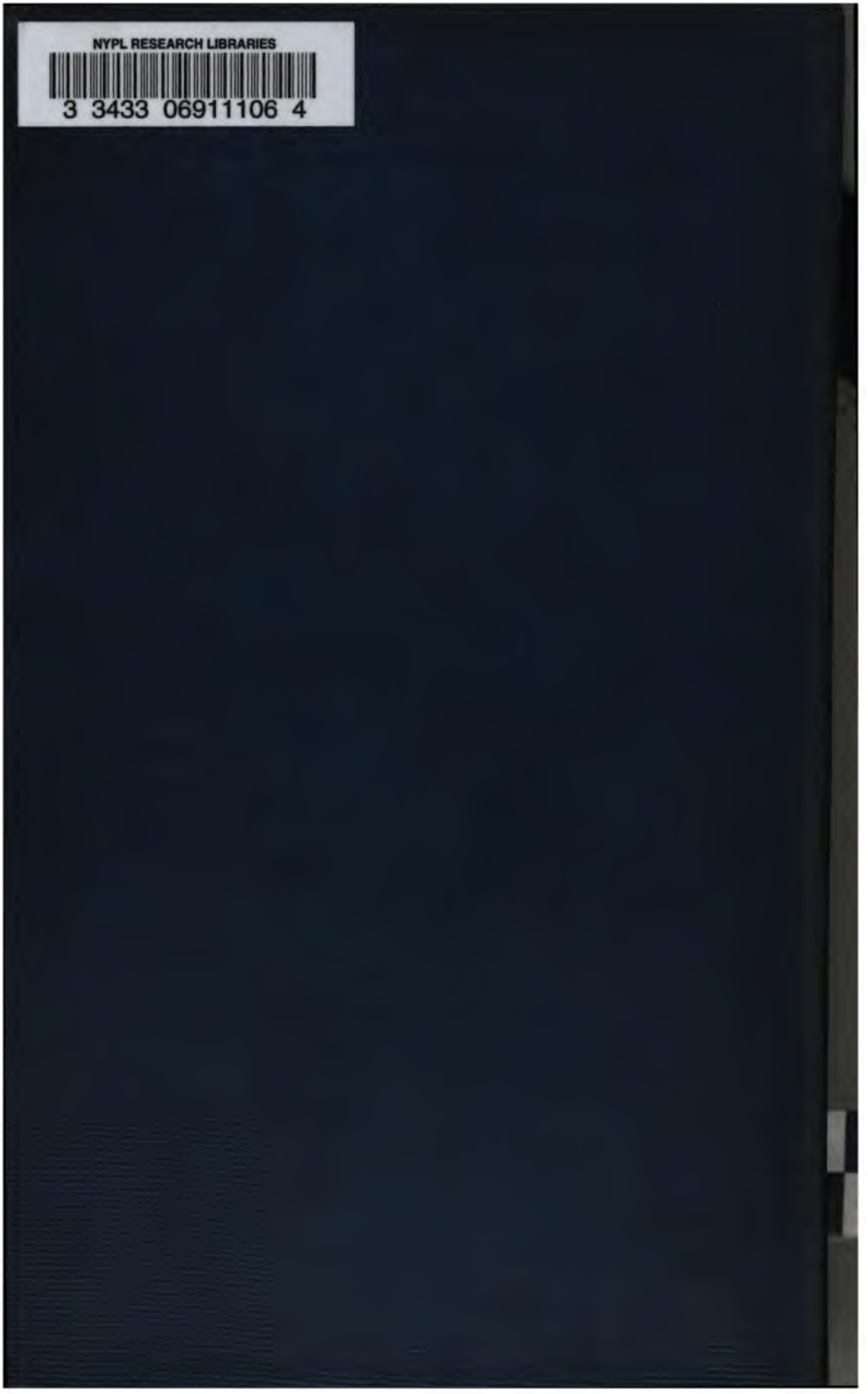
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THE ELEMENTS

OF

ELECTRO-CHEMISTRY

TREATED EXPERIMENTALLY

Luepke

THE ELEMENTS

OF

ELECTRO-CHEMISTRY

TREATED EXPERIMENTALLY

BY

DR. ROBERT LÜPKE

Headmaster of the Municipal Dorothea Realgymnasium, and Lecturer in the Imperial School of Posts and Telegraphs, Berlin

SECOND ENGLISH EDITION

REVISED AND AUGMENTED FROM THE FOURTH GERMAN EDITION BY

M. M. PATTISON MUIR, M.A.

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PREFACE

TO THE FIRST EDITION.

THE researches in physical chemistry which have been prosecuted with great eagerness during the last two decades have led to results whereby many of the problems of exact science which had remained unsolved have been answered. For instance, a deeper insight has been obtained into the nature of solutions, by the work of van't Hoff, who has shown that the law of Avogadro, which had been applied only to gases, holds good also for substances in solution. This result has been of especial importance to electro-chemistry, although at first sight it appears to have no connection with that subject. It may be affirmed to-day that the conduction of the galvanic current in electrolytes, as well as the origin of the current in galvanic cells, matters which had been discussed for a century, have been explained.

The science of electro-chemistry is set forth in detail in researches published in various journals, and in the text-book-

of physical chemistry of Ostwald and Nernst. Nevertheless I have undertaken to write this short book, because I thought the time to be opportune for bringing together the new results in a condensed form, and for giving a short survey to those who are not in a position to make an exhaustive study of the voluminous literature of the subject for themselves. In order to make the theories, which are difficult in themselves, more easily intelligible to the reader, who is assumed not to have more than a knowledge of the fundamental conceptions of physics and chemistry, the various laws have been deduced directly from the experimental results. Mathematical discussions have been introduced for the purpose of more complete confirmation only in a very few cases.

The experiments which form an essential part of this book are carried out with the simplest possible apparatus.* They are arranged to make the process that is under consideration clearly intelligible, and also to ensure the attainment of the final result in as short a time as possible. For this reason they may be made especially useful for teaching, and also for becoming practically acquainted with the physical and chemical properties of various substances. It is true that very accurate results are not to be expected in the experiments wherein measurements are made; for more delicate instruments, such as are to be found only in scientific laboratories, are required in order to obtain accurate numerical results; but, at the same time,

* ...h of the apparatus may be prepared by the student himself. ... be obtained from Glass-blower Max Stuhl (Berlin, N., ...).

such instruments are not generally suitable for the purposes of demonstration.

Although the main purpose of the book is to set forth the purely scientific aspects of electro-chemistry, the practical sides of the subject have not been left altogether unnoticed. Technical electro-chemical processes, and especially the processes of electro-metallurgy, which are so important at present, are referred to in their proper places.

ROBERT LÜPKE.

BERLIN, *May 1st*, 1895.

PREFACE

TO THE SECOND EDITION.

A SECOND Edition of my "Elements of Electro-chemistry, treated experimentally," was called for a few months after the appearance of the book. This showed me that there was want of a book setting forth succinctly the most important parts of electro-chemistry, and that the method of the book, which deduces the laws and elucidates the theories from the basis of experiments, had met with approval. Several works on electro-chemistry, it is true, have appeared in the course of a year, such as those of Ostwald, Jahn, Le Blanc, and Ahrens, to which my "Elements" are much inferior, looked at from the scientific standpoint. Nevertheless I hope that those readers who wish to make a preliminary survey of electro-chemistry before they enter on the study of the more detailed works will receive the second edition of my book with favour.

So far as time allowed, I have enlarged the first edition here and there, and made it more complete. The chapter

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THE ELEMENTS OF ELECTRO-CHEMISTRY.

INTRODUCTION.

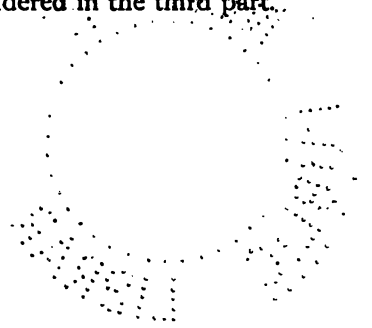
A HUNDRED years have passed since the discovery of the voltaic battery, that simple apparatus which has been the starting-point of all those instruments wherein galvanic currents are obtained by combining conductors of the first and second class. But although voltaic batteries have been used for so long a time it was not until quite recently that the theory of their action was made clear; for the theories that had been advanced, the contact theory and the chemical theory, did not suffice to give a satisfactory explanation of the production of the galvanic current.

Nernst was the first to give a clear representation of the mechanism of the formation of the current by his *osmotic theory*, put forward by him at Göttingen in 1889.

The theory of Nernst is based on a broad and firm foundation. It assumes certain other theories, also of recent date, which are concerned with the most important parts of the youngest branch of scientific chemistry, to wit physical chemistry. It takes especial account of Helmholtz's theory

of current-conduction, Arrhenius' theory of electrolytic dissociation [or ionisation], and van't Hoff's theory of solutions. These theories have all found their proper acknowledgment everywhere at the present time, not only because they rest on sufficient empirical observation, but also because they have most thoroughly explained many physical and chemical phenomena which had before been obscure.

These theories will be dealt with in the first and second parts of this book, and Nernst's theory of current-production will be considered in the third part.



PART I.

RECENT THEORIES OF ELECTROLYSIS.

THE term *electrolysis* refers to the chemical changes which occur when an electric current passes through a *conductor of the second class.* Such a conductor, which is always a chemical compound either in solution or fused, is called an *electrolyte* (λύω = loose). *Conductors of the first class,* which, in the form of wires or plates, lead the current into, or away from, electrolytic cells, are called *electrodes* (ὁδόω = lead in), one being called the *anode* and the other the *kathode* (ἡ ἄνοδος = the way up; ἡ κάθοδος = the way down). The two latter terms are derived from the supposition that the earth's magnetism is caused by electrical currents which flow around the earth parallel to the degrees of latitude, in the direction from east to west, that is from the rising to the setting sun. Because of the difference of potential that is caused on the electrodes by the electrolysing current, the two essentially distinct particles of the electrolyte move in different directions, one towards the anode and the other towards the kathode. These minute particles, which travel in the directions just indicated, are called *ions* (ἰών, *gen.* ἰόντος, = going); *anions* being those which go to the anode, and *kations* those which go to the kathode. The chemical changes brought about by the ions at the electrodes are called electrolysis. As we shall see in the first chapter, the results of these changes may differ very much, according to the conditions that prevail.

[illegible]

[illegible] has [illegible] with a [illegible] pipe, [illegible] of magnesium chloride, [illegible] Potassium-magnesium [illegible] in a platinum dish, [illegible] is obtained in the fused [illegible], on the water-bath in a [illegible] crystallised magnesium [illegible] chloride, with addition of [illegible], and then rapidly heating the [illegible] by a Bunsen flame. The fused mass is poured [illegible] in the [illegible] (*p* in fig. 1), which has [illegible], and which is supported in a [illegible]

[illegible] accumulators* arranged *in series*

* Accumulators made by W. A. Hirsch & Co. (Berlin S.O. Köpenicker Strasse 1941) are very suitable for laboratory purposes. The plates [illegible] consist wholly of a mass of active material enclosed [illegible]. I employ cells 22 centims. high, 12 centims. wide, [illegible] and 9 × 6 × 4½ inches]. When discharged continuously [illegible] they give 60 ampère-hours, if discharged *with* [illegible] hours if a current of 5·6 ampères is taken. [illegible] clous, very considerable; the null effect (*see* [illegible] ampère-hours to 91 per cent.

(that is, one behind the other) is then sent through the fused salt, a knitting-needle which is passed through the stem of the pipe serving as kathode (*k* in fig. 1), and a rod of carbon which dips into the bowl being used as anode (*a* in fig. 1). Although the heat produced by the current soon liquefies the salt, yet it is better to place a small flame beneath the bowl of the pipe.

Chlorine is easily detected by bringing a piece of moistened litmus paper near the anode [the paper is bleached by the chlorine]. But the greater part of the magnesium burns on the surface of the fused salt, which gradually fumes and sputters, and when the apparatus is allowed to cool the magnesium is disseminated through the mass in such fine powder that its silvery lustre cannot be observed. Both drawbacks are easily obviated by covering the fused electrolyte with a thick layer of finely powdered wood charcoal, immediately after closing the circuit. The ·ing is thus avoided, and after allowing the current to ɔr barely twenty minutes a great many lustrous pellets ıagnesium, from 1 to 2, and sometimes even 5, mm. ıeter, can be obtained when the cold mass is broken The pellets should be isolated by rubbing the mass

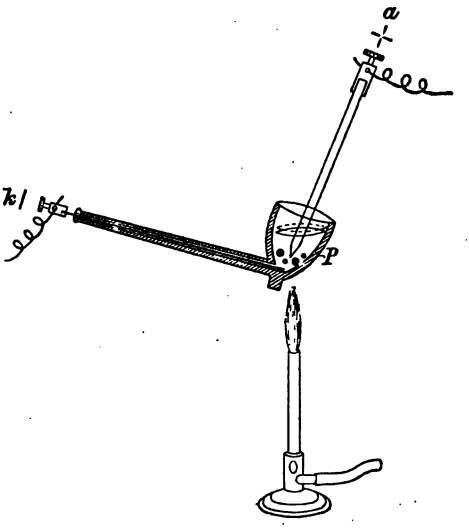


Fig. 1.

[illegible] [illegible] [illegible] [

heated by a large Bunsen lamp. After some time aluminium chloride is deposited in the wide neck of the receiver (*h*) as a white sublimate, and when the action has proceeded for two or three hours the deposit of chloride is removed by means of a knife. As aluminium chloride is very hygroscopic, the salt must be transformed into the more stable double chloride as soon as it is removed from the neck of

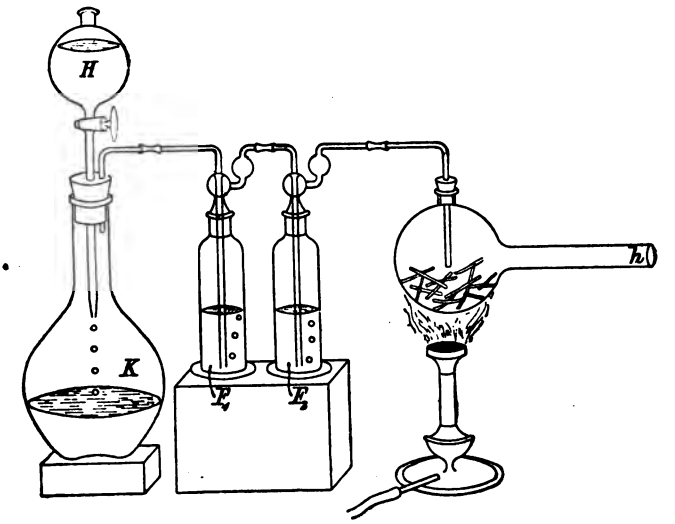


Fig. 2.

the receiver. For this purpose all that is required is to melt two parts of potassium chloride in a platinum crucible, and to add one part of aluminium chloride, in successive portions, constantly, and then to pour out the melted mass on of porcelain. The double salt must be kept in stoppered jar.

rinciple of the experiment wherein the double m-potassium chloride is electrolysed is the same as

filled with gas. The current is stopped, the electrodes are removed, the jar is depressed in the water, and the stopcock is opened; an inflammable gas escapes. This gas, like that made by passing steam over white-hot charcoal, and known as *water-gas*, is a mixture of hydrogen and carbon monoxide; it is formed as shown by the equation—

$$H_2O + C = H_2 + CO.$$

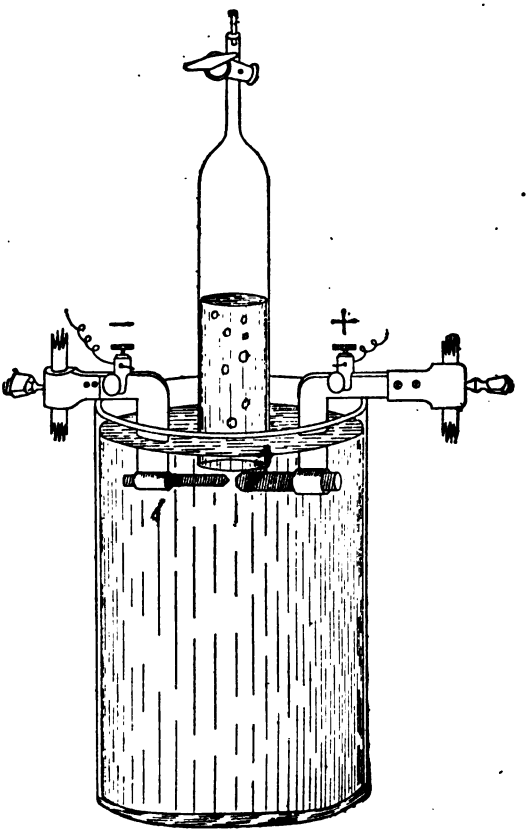


Fig 3.

The decomposition of the water produces hydrogen and oxygen; the latter combines with some of the carbon, whereof the electrodes are formed.

Fused lead chloride is much more easily decomposed by the current than compounds of magnesium or aluminium, and, for this reason, the lead salt is more suitable for the purpose of demonstration. As lead chloride is somewhat volatile when heated, the salt ought to be melted in a porcelain

crucible, in a draught place, before it is put into the bowl of the pipe. A sufficiently large regulus of lead is obtained by passing the current from five accumulators for about ten minutes. The melted regulus is poured out on to a piece of porcelain, and the metallic surface is exposed by rubbing with a file.

Potassium hydroxide is the most suitable base to electrolyse in the molten state. Sufficient mercury is poured into a platinum basin to cover the bottom of the dish; a few sticks of potash are placed in the basin, and these are melted by heating the vessel by a small flame; the current from about five accumulators is then sent through the melted potash, the basin being used as the kathode, while a piece of platinum foil sunk into the electrolyte serves as the anode. The decomposition proceeds in accordance with the scheme $2\ KOH = 2\ K + H_2O + O$. The potassium alloys with the mercury, and the oxygen passes off from the surface of the platinum foil. After about half an hour the liquid amalgam is poured into a test-tube, where it is allowed to solidify. It is easy to prove the presence of potassium by placing the alloy in a small flask arranged for preparing a gas, adding diluted hydrochloric acid, and collecting the hydrogen that comes off; about half a litre of hydrogen may be obtained in a short time.

As lead and chlorine may be separated from fused lead chloride, so the two constituents of zinc chloride, zinc and chlorine, can be obtained by the decomposing action of an electric current on a *concentrated aqueous solution* of the salt zinc chloride. The electrolysis is conducted in a bulbed U-tube, containing two platinum plates [connected with platinum wires which pass through the U-tube], the limbs of the tube being about the length and diameter of ordinary test-tubes. (*See* figure 4.) If ten accumulators are employed,

the bulb of the U-tube will be filled with elegant, branching crystals of zinc, after about twenty minutes; and if a piece of litmus paper is held in the limb of the tube which contains the anode, the paper will be bleached, very quickly, by the chlorine that is coming off.

If the anode is made of the metal of the salt which is electrolysed, the anode will be gradually dissolved by the anions that are separated in contact with it, and, at the same time, the metallic ions of the salt will be deposited on the kathode. Such a separation of metal is shown very prettily by electrolysing an aqueous solution of stannous chloride under the following conditions. The decomposition is effected in a large cylindrical vessel open at both ends (*c* in figure 5), of from 1½ to 2 litres capacity, placed on a tripod; a cork is fitted into the bottom opening of the cylinder, and a copper wire passing through this cork is connected with the anode, *a*, which is a plate of cast tin about 7 centims. broad. The kathode, *k*, is a flat-bottomed copper basin, supported from the cover closing the upper end of the cylinder by the wire for the conduction of the current, which wire is soldered to the basin. The electrolytic liquid is prepared by dissolving 65 grams of stannous chloride in warm hydrochloric acid, removing the excess of acid as far as possible by evaporation, and diluting with water to 1·5 litres. The intensity of the current is regulated so that hydrogen does not make its appearance on *k*. When the circuit is closed tin begins to separate in lustrous filaments, which grow visibly from the bottom of the basin *k* downwards through the liquid.

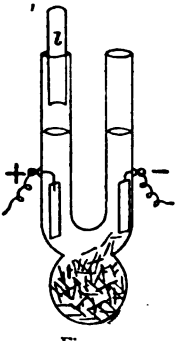


Fig. 4.

Figure 5 represents the appearance of the filaments of ti-

after the current has been passing for about twenty minutes. Branches grow at right angles to the primary filaments. At first these branches are equally large on both sides; but soon the growth of the branches takes place chiefly on one side, and as both the stems and their branches continue to increase in length, new branches appear, in a regular way, between those that have been formed already. Meanwhile the process of branching repeats itself in the branches which were first produced. One of these branches becomes larger than the others, and as the increase of the ramifications becomes slower, this branch stretches in the direction of the stem, and the process begins anew. In this way the formation increases downwards in a regular manner, until, when the anode is nearly reached, the weight of the branches causes [illegible] stem, and the whole falls down. [illegible] and there fall in the [illegible] new stems are formed, [illegible] third of the cylinder [illegible] anions.

[illegible] ions of lead salts [illegible] metal in tree- [illegible], fig. 6, which [illegible] the bottom of [illegible]; this glass is [illegible] with an isolating [illegible] end of a strip of [illegible] a glass of [illegible] from the leaden [illegible] out of 100 grams [illegible] with 100 grams

nitric acid (sp. gr. 1·16). As soon as a current from 5 to 10 accumulators is sent through the liquid, numerous ribbon-shaped, lustrous masses of lead stretch downwards from the kathode, and gradually increase in size.

There are not many electrolytic solutions from which both ions can be separated on the electrodes by a process of electrolysis. The solution of stannous chloride we have been considering is an example of such an electrolyte. Hydrochloric acid also belongs to this category; the volumetric electrolysis of this compound is well known to be important in establishing the fundamental chemical conception of equivalency. This electrolysis is carried out, by Hofmann's method, in a U-tube, which is attached to an upright tube, [illegible] with a [illegible] topcocks, [illegible] electrodes [illegible] *compare* fig. 17, [illegible]er, dif-

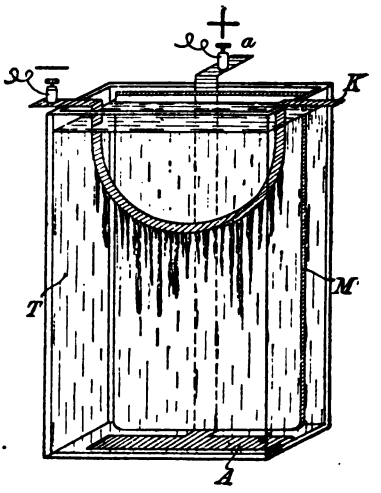


Fig. 6.

[illegible]y equal volumes of gas in the two [illegible]his is due partly to the solubility of the disengagement of oxygen from the [illegible]ty increases the more dilute the electro- After many trials, a satisfactory result [illegible]rolysing, in a Hofmann's apparatus with from pure gas-coke and provided with [illegible] were soldered on, a mixture of 10 c.c. [illegible]id of specific gravity 1·125 and 150 c.c

very concentrated solution of calcium chloride of specific gravity 1·36. After allowing the current from five accumulators to pass for fifty minutes, the stopcocks being open, the liquid in the limb which contained the anode was quite saturated with chlorine; and when the stopcocks were then closed exactly 40 c.c. of chlorine were obtained for every 40 c.c. of hydrogen produced. It is necessary to guard against the possibility of a negative gaseous pressure by removing liquid from the upright tube, after closing the stopcocks in the two limbs, either by the use of a siphon, or, preferably, by means of a stopcock let into the lower part of the upright tube. The apparatus described by Lothar Meyer (*Berichte der d. Chem. Ges.*, **27**, 850 [1894]) depends on the same principle, and this apparatus has the advantage of employing pure hydrochloric acid as the liquid to be electrolysed.

Hydrogen and chlorine also appear at the electrodes in the electrolysis of a solution of common salt; the chlorine separates directly at the anode, and the hydrogen separates indirectly at the kathode, for each sodium ion turns out an atom of hydrogen from a molecule of water, so that soda is formed in the neighbourhood of the kathode ($Na + H_2O = NaOH + H$). Attempts have been eagerly made to turn this reaction to account in chemical technology, and so to obtain the products of the [illegible]-industry in a simpler way. The most important part of [illegible]roblem is the construction of a suitable diaphragm for k[illegible]eparate the substances that are produced at the two [illegible]s. Although this difficulty has not yet been co[illegible]vercome, the electrolysis of solutions of common s[illegible]n conducted in several places on a large scale, [illegible]ally for bleaching purposes.

[illegible]trical [illegible]of bleaching is easily understood from ing [illegible] The four-sided vessel of a Böse [illegible]or [illegible]nd note p. 4) is used as a cell

Three longitudinal grooves are cut in the thin side-walls of the vessel; a clay diaphragm is placed in the middle groove, and a plate cut from retort carbon, and provided with a binding screw, in each of the other grooves. A piece of red-dyed cotton is spread, by means of four little wooden pegs, on that carbon plate which is to be used as the anode. The electrolytic liquid, which is poured into the cell, is made by dissolving 50 grams of common salt, 5 grams of magnesium chloride, and a few drops of hydrochloric acid, in a litre of water. The cell is covered with a glass vessel, and the poles of a battery of five accumulators are placed on the electrodes; in a short time so much of the red cotton as is immersed in the liquid is completely bleached.

Chlorate of potassium is made in certain factories by the electrolysis of a solution of potassium chloride, the basic lye which is formed around the kathode being transported from time to time to the anode, where, at the higher temperature, the chlorine reacts in accordance with the equation

$$6KOH + 6Cl = KClO_3 + 5KCl + 3H_2O.$$

Most of the electrolytes that have been referred to are binary compounds, and in the majority of the cases mentioned the two constituents of the electrolyte separate directly at the electrodes. *Such a separation in two directions generally occurs as a consequence of electrolysis, however complicated the molecule of the electrolyte may be.* The hydrogen, or the metal, or a radicle which represents the hydrogen, is always carried towards the kathode, by the primary reaction, and the rest of the molecule travels towards the anode. Then, either the ions are set free on the electrodes, or secondary reactions occur thereat, between the ions and the substances of which the electrodes are made, or between the ions and the electrolyt or the water. The occurrence of these secondary reactior

will be better understood by considering the following examples.

If a current of moderate intensity is sent through a concentrated solution of copper sulphate in a rectangular trough, copper electrodes being used, that part of the kathode which is immersed in the liquid is soon covered with a dull red deposit of copper, and the mass of the anode diminishes because each SO_4 ion dissolves an atom of copper. The result of the passage of the current is, therefore, merely to carry copper from the anode to the kathode.

The fact that the weight of the copper plate increases or decreases according as the plate is made the kathode or the anode may be demonstrated by Langley's experiment (*Zeitschrift f. physikal. Chemie*, **2**, 83-91 [1888]), wherein the electrode in question is attached to one end of the beam of a balance in such a way that the swinging of the beam is not interfered with. Figure 7 represents a suitable arrangement. *T* is a funnel-shaped metallic vessel used as a counterpoise; the copper electrode, p_1, which is 8 centims. long by 3 centims. broad, is suspended by the platinum wire p on the hook h, and is completely immersed in the electrolyte (200 c.c. of a solution of copper sulphate mixed with 15 c.c. of sulphuric acid) contained in the cell *Z*; the electrode hangs freely so that it can move up and down without touching the sides of the cell. *K* is a commutator the binding screws of which are connected on the one hand with a battery, consisting of two accumulators, on the other hand with the kathode, and with the plate of copper which is placed securely in the cell. The balance is brought into equilibrium by placing weights on the negative pole of the battery side. After about three minutes the beam is lowered where the cell is placed. The

current is then reversed; after three minutes the beam again attains equilibrium, and after another three minutes it inclines in the opposite direction.

The experiment of electrolysing a solution of copper sulphate between copper electrodes illustrates the principle of electroplating, and also the principles of the electrical

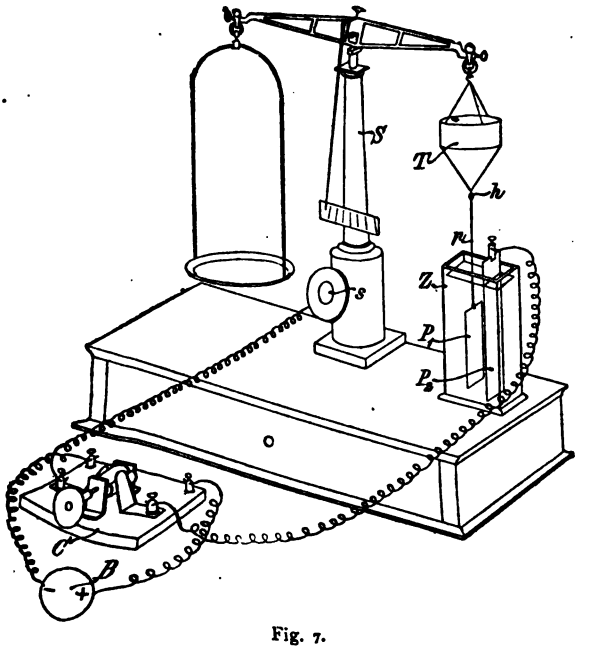
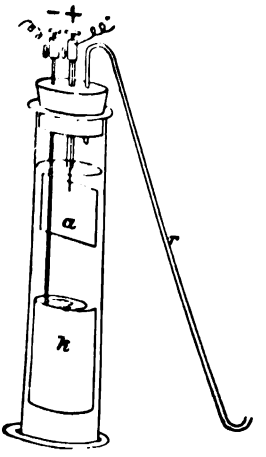


Fig. 7.

tion of crude copper and the electrical separation
er from anodes of copper ore. (For more details
III., Chapter VI.) The experiment also elucidates
anical art of the galvanic etching of iron or copper
The vessels are covered with a non-conducting
arnish, and are then arranged as the anodes in
opper sulphate baths, after the pattern to be etche

has been cut through the covering of varnish. The deeply etched parts of the vessels can then be filled with other metals (silver, gold, etc.) by placing the vessels, as they are taken from the copper baths, as kathodes in baths of the metals to be deposited; an imitation of Oriental inlaid metal-work is thus produced.

The kind of etching that has been described is easily carried out on a small scale. A plate of polished copper is covered with melted wax, by the use of a pencil; a pattern is then cut through the wax by a knitting-needle, and the plate is exposed for about twenty minutes as the anode [in an acidified bath of a copper salt] to the action of a current from four cells. When the wax is then removed by turpentine, the pattern is seen eaten into the plate.



. 8.

If the copper anode in an acidified copper bath is replaced by a plate of platinum, oxygen is disengaged on the platinum, in accordance with the equation

$$SO_4 + H_2O = H_2SO_4 + O;$$

mical affinity of the platinum does not cause the f a sulphate under these experimental conditions. olytic pro suitable for preparing small of oxygen paratus of Landolt, represented being u kathode, *k*, is a spirally rolled atinum; of platinum which is soldered nduct: rent is covered with an isolating The node is marked *a* in the figure, he ng off the gas.

Figure 9 represents an apparatus used for demonstrating that hydrogen is set free on the platinum kathode, *k*, when a dilute solution of sulphuric acid (1 : 8) is electrolysed, and that the ion SO_4 causes solution of copper from the copper anode, *a*, although copper does not otherwise dissolve in diluted sulphuric acid at the ordinary temperature. When a current from five accumulators has been passing for about

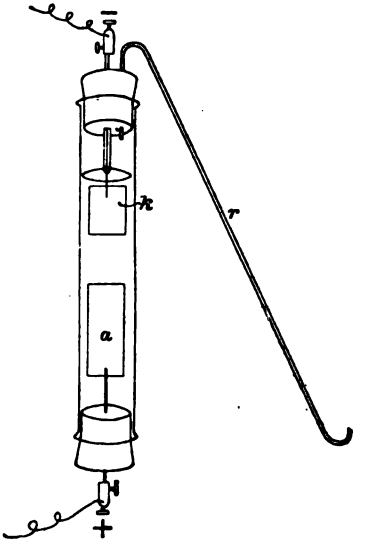


Fig. 9.

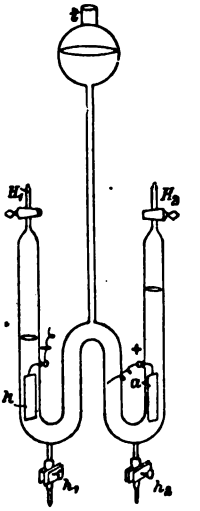


Fig. 10.

ten minutes, the liquid around the electrode *a* becomes ... ctly blue, and pure hydrogen escapes by the tube *r*.

... acids and salts are decomposed by electrolysis, ..., into hydrogen, or metal, and acid radicle.

... ysalts of the alkali metals seem, at the first glance, ... eptions to this rule. If a cold concentrated solu- ... otassium sulphate is electrolysed, in the apparatus ... l by figure 10, between the platinum electrode ... e current from ten accumulators being employe

(potassium sulphate or sodium chloride), to which a few drops of an alcoholic solution of phenolphthaleïn have been added. When the circuit is closed the liquid round one of the electrodes becomes coloured rose-red: that electrode is in connection with the negative pole of the battery which is being examined; for free alkali is formed at this electrode, and reacting with the phenolphthaleïn forms the red alkali salt of that [slightly acidic] compound. If the cylinder is shaken the red colour disappears, for the acid produced at the anode decomposes the salt and sets free phenolphthaleïn.*

The use of "*pole-reagent paper*" is based on these reactions. That reagent is blotting-paper soaked in potassium sulphate solution mixed with a very little solution of phenolphthaleïn; it must be moistened before use. The reaction is more delicate if the paper is impregnated with starch paste (2 : 100) to which has been added one part of potassium iodide and a very little phenolphthaleïn, then dried in air free from dust, and kept in a stoppered glass bottle. When the poles are laid on this paper the negative pole is recognised, as before, by the production of a red colour, and a very dark blue colour is produced on the paper under the positive pole because of the formation of "iodide of starch" by the iodine set free by the current. This paper enables an operator to recognise the sign of one of the two poles of a battery when the other is led to earth, as is often the case in telegraph offices; it is only necessary to lay the moistened paper on a conductor connected with the earth, and to touch it with the doubtful pole. The action of this reagent may be made clear to a larger audience by passing a current through the

* According to Ostwald (see *Foundations of Analytical Chemistry*, 118), the alkali salts of phenolphthaleïn are ionised in dilute solutions, and the red colour is caused by the free ions; when an acid is added un-ionised phenolphthaleïn is formed, and this is colourless.—[TR.]

Daniell gave an explanation of the electrolysis of salts which was free from objections. He said that the current decomposes potassium sulphate, as it decomposes every other salt, between platinum electrodes, into metal and acidic radicle: but in the case of potassium sulphate both these products of decomposition enter into secondary reactions with the water; the potassium reacts at the kathode in accordance with the equation

$$2K + 2H_2O = 2KOH + H_2$$

and the SO_4 reacts at the anode in this way—

$$SO_4 + H_2O = H_2SO_4 + O.$$

The gases that are given off are, therefore, secondary products; and it is thus explained why the volumes of both gases are equal to the volumes of the same gases obtained in the voltameter, and are also equivalent to the quantities of acid and base observed at the electrodes. It is possible to separate potassium directly from solutions of its salts, because if mercury is used as the kathode the potassium forms an amalgam with that metal, and the action of water on this amalgam becomes apparent, by the evolution of little bubbles of hydrogen, only some time after the closing of the circuit.

The separation of potassium on the kathode is effected by removing, as far as possible, the action of the water used as a solvent. Nernst (*Zeitschrift für Elektrochemie*, 3, 308 [1897] describes the following lecture-experiment. R. (fig. 12) is a test-tube (12 centims. long, by 1½ wide), to the bottom of which is fused a tube, *r*, 2 mm. wide, bent thrice at right angles. The cork K carries (1) the little tube *h*, open at both ends, for the escape of the gas coming from the anode; (2) the funnel T (25 c.c. capacity), the neck

towards metals (its occlusion), show that hydrogen is to be looked on as a metal, and as the hydroxyl groups of the bases correspond with the acidic residues of salts, acids and bases may be included in the class of salts. Looking at the subject from this point of view, Hittorf made the following generalisation (*Über die Wanderungen der Ionen*, 2 Hälfte, p. 124 [*Ostwald's Klassiker*]: *Electrolytes are salts; they are separated by electrolysis into the same atoms, or atomic groups, as they exchange in their chemical reactions with one another.* All other substances, whether they be themselves liquids or whether they be dissolved, are non-conductors. This statement especially concerns the majority of the organic compounds, for it is only those organic compounds that have a salt-like character, in the meaning given to this term by Hittorf, which conduct the electric current.

Water is never primarily decomposed when a current is passed through aqueous solutions of electrolytes. Indeed, absolutely pure water does not conduct it all. The statement, which is made so often, that the sulphuric acid added to the water in a voltameter makes the water conduct, is only correct in so far that the acid separates, primarily, into H_2 and SO_4, and that the SO_4 ion is then reconverted into H_2SO_4 by reacting with the water and splitting off oxygen. One ought to speak of this reaction as an electrolysis of sulphuric acid. The addition to the water of some other oxyacid, or of a soluble base, or even of an alkali salt, makes it conduct, just as the addition of sulphuric acid enables the current to pass. The conductivity of naturally occurring water is to be attributed to the presence of alkali

[illegible] conclusion, it is to be observed that the electrolysis [illegible] acidified with sulphuric acid follows a somewha

the positive pole of a battery of about five accumulators is connected with the wire in g_1, and the negative pole with the wire in g_2, hydrogen escapes by the narrow tube near g_2, and oxygen through r, and the presence of ozone in the oxygen is detected by the blue colour which is very quickly produced if the gas is caused to bubble through a solution of potassium iodide mixed with starch paste placed in the beaker-glass. The quantity of ozone increases considerably if some chromium troxide is added to the electrolytic liquid, and the apparatus is immersed in a freezing mixture.

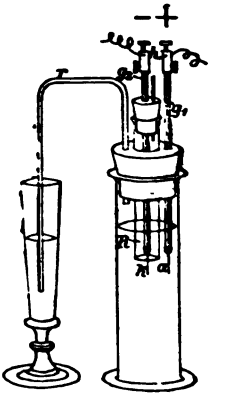


Fig. 13.

This experimental arrangement may be used to show the production of hydrogen peroxide, besides ozone, during the electrolysis of dilute sulphuric acid. Considerable quantities of hydrogen peroxide are obtained by letting the current pass for half a minute through a mixture of 80 grams H_2SO_4 and 20 grams H_2O. A solution of 1 gram titanic acid in a hot mixture of 70 grams H_2SO_4 and 30 grams H_2O is used as a test for hydrogen peroxide; 3 c.c. of this solution are added to the electrolyte and the peroxide is recognised by the deep yellow colour it produces.

That the ions can react with the electrolytes themselves may be proved by a great number of examples. The following cases will suffice to show how greatly the results of electrolytic processes may be varied by secondary reactions of this kind.

There is a well-known method for preparing nitrogen chloride by electrolysing a solution of salammoniac betwe

a mercury kathode and a platinum anode (Heumann, *Anleitung zum Experimentiren*, p. 268 [1893]); the chlorine which is produced at the anode in that process reacts with undecomposed salammoniac in accordance with the equation

$$NH_4Cl + 6Cl = NCl_3 + 4HCl.$$

The electrolysis of a solution of ammonia is more complicated; the process may be represented by the scheme

$$\begin{array}{r|l} 6(NH_4) & 6(OH) \\ 6NH_4 + 6H_2O = 6NH_4OH + 6H & \begin{array}{l} 6(OH) = 3H_2O + 3O \\ 2NH_4OH + 3O = 5H_2O + 2N. \end{array} \end{array}$$

The radicle NH_4 interacts with water similarly to potassium, and six volumes of hydrogen are produced at the kathode. The oxygen which is separated from the 6(OH) ions oxidises two molecules of ammonium hydroxide to water and nitrogen; and thus it is that the volumes of hydrogen and nitrogen produced are in the ratio of 3 to 1. The experiment is best carried out in the apparatus used for the electrolysis of hydrochloric acid. Inasmuch as the
·n which is set free dissolves fairly easily in ammonia
ı, it is best to employ as electrolyte a mixture of
· concentrated solution of common salt and 20 c.c.
:rated ammonia solution, and to allow the current
ix accumulators to pass through the apparatus for an
before the stopcocks of the two limbs are closed
he stopcock of the upright tube is opened (*see* fig. 17,
').

hen an alkaline solution of a lead salt is electrolysed,
xygen produced at th e result of secondary

ctions, oxidises the lead compound to lead dioxide, as own in the following equations:—

$$Pb(NO_3)_2 = Pb + 2NO_3,$$
$$2NO_3 + H_2O = 2HNO_3 + O,$$
$$Pb(NO_3)_2 + H_2O + O = 2HNO_3 + PbO_2.$$

e experiment is easily performed. The glass basin S_1 g. 14), in the tubulus of which, *t*, is fastened the wire is placed on a triangle, and is filled with a 5 per cent. ution of lead nitrate mixed with its own volume of normal solution of caustic soda [a normal solution ntains 40 grams of NaOH per litre]; metallic plate, preferably a platinum sin, S_2, is immersed in the liquid in the ss vessel. When *k* has been connected h the kathode pole and *a* with the ode pole of an accumulator, for about een seconds, four or five iridescent, nbow-coloured rings of lead dioxide pear on the platinum basin, S_2. The art of colouring tals, which aims at ornamenting vessels of copper or ss that have been thinly gilt, is based on this reaction. e experiment is finished in less than a minute; if a nganese salt is used the rings of manganese dioxide that formed are more numerous than those of lead dioxide. cobalt sulphate is used instead of manganese sulphate, gs of cobalt oxide do not form until after about twenty nutes.

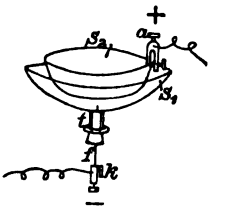


Fig. 14.

The process of electroplating with silver, by the use of a ution of potassium-silver cyanide ($KAgCy_2$), which is such ommon technical operation, is accomplished, according to ttorf *Über die Wanderungen der Ionen*, 2 Hälfte, p. 74 *twald's Klassiker*]), by the following reactions: the kati

potassium (K) travels to the kathode, and the anion $AgCy_2$ to the anode; and each K ion precipitates silver on the kathode in accordance with the equation

$$K + KAgCy_2 = 2KCy + Ag,$$

while the anion $AgCy_2$ dissolves an atom of silver from the silver anode, and these re-form the complex cyanide ($AgKCy_2$) by combining with the 2 KCy [produced in the way shown by the above equation]. If the anode consists of platinum, cyanogen gas is set free thereat from the anion $AgCy_2$, and the platinum becomes covered with silver cyanide [AgCy] which soon stops the current. Hittorf attributes the separation of the silver in a coherent and homogeneous form to the fact that the precipitation on the kathode is the result of a secondary reaction; it is this circumstance which gives its importance to the technical applications of the double cyanide as an electrolyte. For the silver which is separated from a solution of silver nitrate, as the result of the primary reaction of the current, forms branching crystals, which increase downwards, and are easily rubbed off the electrode.

The double potassium-gold cyanide, $KAuCy_2$, is employed in electroplating with gold, as the double silver cyanide is employed in plating with silver. The potassium cyanide process, which is the most recent method, for extracting gold depends on the electrolysis of this gold salt. This process has become so important that the value of the gold extracted by its use in 1894 in the Transvaal amounted to about £7,000,000, which is an output that places that district in the forefront of the gold-producing countries at the present time. The gold, which is found in a very finely divided condition in the rocks, is dissolved by a dilute solution of

tassium cyanide, in the presence of oxidising bodies, in cordance with the equation

$$4KCy + 2Au + H_2O + O = 2KAuCy_2 + 2KOH;$$

d the solution is subjected to electrolysis between steel odes and lead kathodes. Prussian blue, which is again rked up into potassium cyanide, is formed on the anodes; : leaden kathodes, encrusted with gold, are taken to the nace-hearths, whereon the gold remains after the removal the lead by cupellation.

The electrolysis of a solution of potassium ferrocyanide, $FeCy_6$, containing 10 c.c. of a saturated solution the salt mixed with 200 c.c. of water, and dified by hydrocyanic acid, shows how compli- ed the secondary reactions in an electrolytic ess may become. The current from five umulators is passed through the solution placed ween platinum electrodes in a U-tube (*see* fig. . After about twenty minutes, Prussian blue, $_2)_2(FeCy_6)_3$, has formed in the anode limb, ile the liquid in the kathode limb is milky n small uprising bubbles of hydrogen.

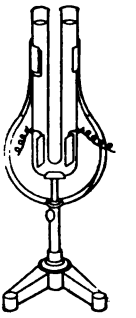


Fig. 15.

cording to Hittorf (*loc. cit.*, p. 72), 4K goes to the kathode, re it reacts with water as shown by the equation

$$4K + 4H_2O = 4KOH + 4H,$$

the ion $FeCy_6$ goes to the anode. If there is a suffi- t supply of K_4FeCy_6, the anion reacts with that pound to produce potassium ferricyanide, K_3FeCy_6 rding to the equation

$$3K_4FeCy_6 + FeCy_6 = 4K_3FeCy_6.$$

[redacted]

[redacted]

[redacted]

and the ion $FeCy_6$ goes to the anode. If ...
cient supply of K_4FeCy_6, the anion ...
compound to produce potassium fer...
according to the equation

$$3K_4FeCy_6 + FeCy_6 = \ldots$$

But if the solution is as dilute as that mentioned above, the following processes occur at the anode :—

$$FeCy_6 + 2H_2O = H_4FeCy_6 + 2O,$$

and $$7H_4FeCy_6 + 2O = 24HCy + (Fe_2)_3(FeCy_6)_2 + 2H_2O.$$

The electrolysis of a concentrated solution of sodium acetate, $CH_3.COONa$, produces a combustible gas at each electrode. A cylinder of about one litre capacity, such as was used by v. Hofmann in his lectures, serves as the decomposition-cell (*see* *C*, fig 16). The porous cell *z* is placed in this cylinder, and over the upper edge of the

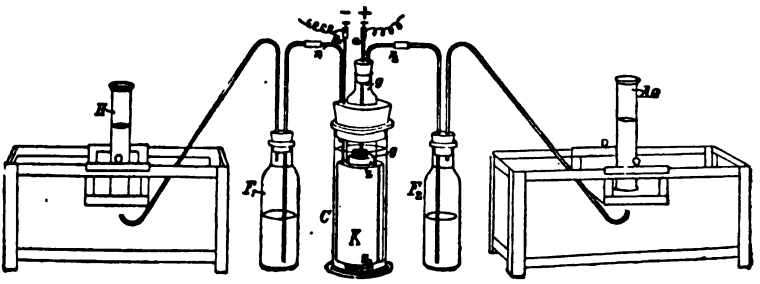


Fig. 16.

cylinder is inverted the bell-shaped vessel *g* (made by cutting off the bottom of a flask). The cylindrical piece of copper foil *K*, which is soldered to the conducting strip *k*, is the kathode ; and the platinum plate fastened to the wire *a* is the anode. The exit tube for gas r_1 is connected with a flask, F_1, containing water ; and the exit tube r_2 is connected with another flask, F_2, of the same size, but containing a volume of baryta water equal to the volume of water in F_1. All the corks must, of course, fit very tightly. The current five accumulators is sufficient for the experiment. produced in the secondary reaction

$$2Na + 2H_2O = 2NaOH + 2H,$$

escapes by r_1. According to Jahn (*Grundriss der Elektrochemie*, p. 292 [1895]), the following processes take place at the anode:

$$2CH_3.COO + H_2O = 2CH_3.COOH + O,$$

and

$$2CH_3.COOH + O = C_2H_6 + 2CO_2 + H_2O.$$

The gases ethane (C_2H_6) and carbon dioxide (CO_2) escape by r_2; the latter gas is absorbed by the baryta water (the absorption is shown by the formation of a white precipitate of barium carbonate in the flask F_2), while the ethane collects in the cylinder *Ae*, placed in the pneumatic trough. The volume of ethane collected is almost equal to that of the hydrogen which is obtained in the cylinder *H* placed in the trough on the other side of the electrolytic cell. The deficit in the volume of ethane obtained is due, according to Jahn, to the oxidation of some of the acetic acid, at the anode, by the oxygen in accordance with the equation

$$CH_3.COOH + 4O = 2CO_2 + 2H_2O.$$

The hydrogen and ethane may be distinguished by the luminosities of their flames; or, better, by the fact that the ethane takes fire quietly, while the hydrogen ignites with slight explosion. The experiment is of especial interest in organic chemistry.

It is to be remarked, in concluding this chapter, that endeavours are being made to turn to account the secondary reactions of electrolytic processes between indifferent electrodes for the practical preparation of organic compounds. If a solution of potassium sulphocyanide (1 : 5) is electrolysed, in the apparatus represented in figure 10 (p. 19), by the current from twelve accumulators hydrogen is given off at the kathode, while the oxygen at the anode oxidises the sulphocyanic acid to *kanarin*, which is a yellow colouring

ase, is subjected to electrolysis. The intensity of the current, he concentration, and the temperature must be regulated n a special way for each preparation. Nitro-compounds, for instance, are reduced to hydrazo-compounds in alkaline olutions, and to amido-compounds in acid solutions.

An example of the oxidising effects of the electric current s furnished by the conversion of aniline into aniline black, n accordance with the equation

$$2C_6H_5NH_2 + O_2 = 2H_2O + C_{12}H_{10}N_2.$$

The experiment may be performed by mixing 100 grams of aniline with 100 c.c. of pure hydrochloric acid (spec. grav. 1·119), dissolving 50 grams of the aniline hydrochloride, which crystallises out on cooling, in 500 c.c. of water, adding 20 grams potassium chlorate, placing this mixture in an electrolytic cell, like that used in the experiment illustrative of electrical bleaching (p. 14), with a piece of white woollen cloth, which has been boiled in dilute soda solution, stretched on the anode-plate, and sending the current from four accumulators through the liquid; after about thirty minutes those parts of the woollen cloth which are in direct contact with the electrode are coloured greenish-black. The electrolytic formation of aniline black may be demonstrated more simply as follows. A mixture of 19 grams aniline and 22 grams toluidine is neutralised by 24 grams glacial acetic acid; the acetate is dissolved in 200 c.c. water, and a few cc. of this solution are placed in the anode-limb of the U-tube shown in figure 15 (p. 31), which is filled to above the electrodes with a concentrated solution of common salt. When the current from six accumulators has passed for a few minutes, the contents of the anode-limb become deep black, because of the reaction brought about by the chlorine which is liberated.

means of which the current is at first diminished, a Hofmann's apparatus for the electrolysis of water, and four glass troughs: the Hofmann's apparatus and two of the troughs are represented in figure 17. The electrode-plates *a* and *k* project downwards in each trough; the conducting wires of these plates are connected by binding screws with the slips of copper *S S*. The kathodes are composed wholly of platinum; they must be cleaned carefully, by fuming nitric acid, and weighed, accurately to a centigram, before the experiment begins. Either platinum, or the metal which is contained in the electrolyte, may be used for making the anode in each cell. In selecting electrolytes, care must be taken that the metals deposited on the kathodes shall adhere firmly to the platinum plates, that these deposited metals shall not suffer oxidation—at any rate, not during the time required for weighing—and that the valencies of the atoms of the metals shall be as different as possible. The following electrolytes are recommended :—

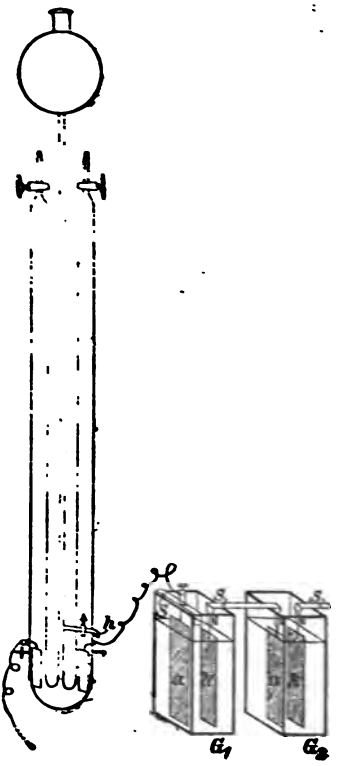


Fig. 17.

(1) A solution of potassium-silver cyanide, obtained by dissolving 3 grams silver nitrate and 5 grams potassium cyanide in 200 c.c. water.

(2) A solution of cuprous chloride, prepared by dissolving 3 grams of the salt sold by the chemical dealers, after washing on a filter with water, in hydrochloric acid, and diluting to 200 c.c.

(3) A solution of copper sulphate, made by adding 100 c.c. water and 15 c.c. nitric acid to 100 c.c. of a saturated solution.

(4) A solution of tetrachloride of tin, prepared by dissolving 1 gram tin-foil in hydrochloric acid, adding a few drops of bromine, evaporating until almost every trace of free acid is removed, and then adding 100 cc water and 100 c.c. of a saturated solution of ammonium oxalate.

The electrolysis is allowed to proceed for about thirty minutes; the kathode-plates are then rinsed with water, dried thoroughly with alcohol and with ether, and weighed. In *Table I.* are given the results of a carefully conducted experiment.

TABLE I.

I. Diluted sulphuric acid (1 : 19).	II. $KAgCy_2$	III. CuCl.	IV. $CuSO_4$.	V. $SnCl_4$.
Pt + Pt	− + Pt Ag	− + Pt Cu	− + Pt Cu	− + Pt Pt
[illegible] mgm. Ag	380 mgm. Cu	190 mgm. Cu	170 mgm. Sn	
[illegible] mgm. Ag	63·6 mgm. Cu	31·8 mgm. Cu	28·3 mgm. Sn	
[illegible]	63·3 + 0·4	63·3 + 0·4	117·8 − 4	

[illegible]ress the weights is of the kations [illegible] referred to a [illegible] unit weight of [illegible]be very nearly th[illegible] ame as the [illegible]ng each atomic weight by the [illegible]olumns II. and III. the c[illegible] I. the silver and

copper atoms are monovalent, in column IV. the copper atoms are divalent, and in column V. the atoms of tin are tetravalent. The law of Faraday is demonstrated satisfactorily by the experiments. Moreover, the results show that the quantities of the kations that have been separated are proportional to the quantity of the current, and also to the duration of the action of the current.

The more accurate experiments of F. and W. Kohlrausch have shown that 0·3281 mgm. of copper was separated from cupric salts by one *coulomb** of electricity; or, that 31·65 grams of copper were separated by 96,465 (in round numbers 96,500) coulombs. This quantity of electricity expresses the *electro-chemical equivalent*, that is to say, the number of coulombs which causes the separation, in one second, of that fraction of the atomic weight of a metal, or of the [formula-] weight of an anion-group, expressed in grams, which corresponds with a single valency.†

The measurement of the intensity of a current [that is, the quantity of electricity which passes through any cross-section of the conductor in one second] by means of voltameters depends upon the exact proportionality between the quantity of electricity and the quantity of the ions that are separated.

* If the unit quantity of electricity, one *coulomb*, flows through any given section of the conductor in one second, the intensity of the current is one *ampère*. The unit of potential, the *volt*, is so fixed that one of electricity is driven by it, per second, through a resistance ', that is, through a column of mercury 106·3 centims. long mm. section (at 0°); the coulomb is so adjusted that 1 volt, that is, the unit of electrical energy, is equal to 10^7 *ergs*. This quantity of energy is called a *watt*.' ment in the text may be put thus. The electro-chemical the number of coulombs that causes the separation of a t of a metal, or anion-group, in one second; a gram- g the quotient obtained by dividing the atomic weight of e formula-weight of the anion-group, taken in grams, b he metal or anion-group.—[TR.]

One coulomb separates 1·1181 mgm. silver, per second, in a silver-voltameter, and sets free 0·174 c.c. explosive gas [hydrogen and oxygen in the ratio of 2 to 1 by volume] (reduced to 0° and 760 mm. pressure) in the same time in a water-voltameter. Supposing that 20 c.c. hydrogen and 10 c.c. oxygen (referred to normal temperature and pressure) were obtained, in an apparatus for electrolysing water, in three minutes, this is equal to a production of 0·1667 c.c. explosive gas per second; and, therefore, the quantity of electricity was 0·1667 / 0·174, that is 0·958 coulomb.

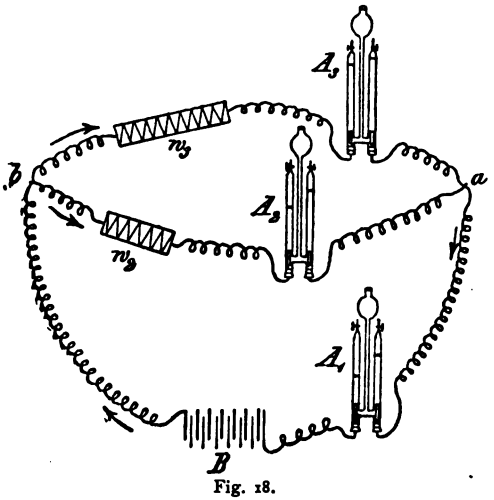


Fig. 18.

If one has three apparatuses of nearly equal size for the decomposition of water, whose resistances are equal (say 10 ohms each), then the law of the division of the current may be experimentally deduced in a few minutes by using the arrangement shown in figure 18 (*see* Grätz, *Die Elektricität und ihre Anwendungen*, p. 127 [1895]). B is a battery of twelve accumulators; the resistance w_2 in the current-path $a\ A_2\ w_2\ b$ amounts to 100 ohms, and the resistance w_3 in the current-path $a\ A_3\ w_3\ b$ to 460 ohms. In an experiment there were obtained 42·5 c.c. explosive gas [mixture of two volumes hydrogen with one volume oxygen] in A_1, 34·5 c.c. in A_2, and 7·5 c.c. in A_3. Hence it follows that

$$i_1 = i_2 + i_3$$

where the quantity of the current passing by the path $b\,B\,A_1\,a$ is represented by i_1, the quantity passing along the path $a\,A_2\,w_2\,b$ is represented by i_2, and i_3 is the quantity passing by the path $a\,A_3\,w_3\,b$. If the resistance of one of the decomposition-apparatuses is expressed by W (the three have all the same resistance), then the equation ought to hold good

$$i_2(w_2 + W) = i_3(w_3 + W).$$

The equation is fairly satisfied by the experimental results; for $i_2\,(w_2 + W) = 379{\cdot}5$, and $i_3\,(w_3 + W) = 352{\cdot}5$. The difference between these values is due to differences between the decomposition-apparatuses A_1, A_2 and A_3.

It follows from Faraday's law that when a quantity of electricity measured by 96,500 coulombs acts on an electrolyte, such quantities of the ions as correspond with a single valency always travel towards the electrodes where the respective actions take place, independently of the chemical affinity whereby these ions are bound together in the undecomposed molecules. The accuracy of the law has been established by H. von Helmholtz even for a current so feeble that a century would be required for it to separate a single milligram of explosive gas from water.

In the *Faraday Lecture* delivered by him in London on April 5th, 1881 [see *Journal of the Chemical Society*, **39**, p. 277], H. von Helmholtz laid the foundations of a new electrochemical theory which explains the facts embraced by Faraday's law.

The most important of these facts may be stated thus: *Every single valency of an elementary or compound ion is charged with exactly the same quantity of positive or negative electricity, which behaves as if it were an electrical atom that cannot be further divided.* When, therefore, the circuit is closed, th kations in the electrolytic cell, being charged positively, a

with the water, then negative hydroxyl ions are formed at the kathode, and positive hydrogen ions are formed at the anode, from the molecules of water, at the cost of the electrolysing current. Consequently, when the anion SO_4 appears at a platinum anode, two positively charged atoms of hydrogen, and also an atom of oxygen, are set free from the molecule of water; and when a potassium ion, or a sodium ion, appears at the kathode, a single hydroxyl group becomes negatively charged at the kathode, and this group plays the part of the anion necessary to the alkali ion, while an atom of hydrogen is disengaged at the kathode.

H. von Helmholtz has thus made clear wherein consists the process of the passage of electricity through a conductor of the second class, which must always be a chemical compound. At the same time, by the hypothesis that equal quantities of electricity cling to ions of equal valency, he has explained why the weights of the substances that are concerned in those chemical changes which are brought about by equal quantities of current electricity, are always in the ratio of the equivalent weights of these substances. Moreover, it is possible to understand how isomeric ions can differ qualitatively, for instance in their colours; why the ferro-ion should be green while the ferri-ion is yellowish-red, or why the MnO_4 ion of permanganic acid ($HMnO_4$) is violet and the MnO_4 ion of manganic acid (H_2MnO_4) is green. The qualities of the ions are dependent on their energy-content, and this, in turn, is conditioned by the number of the valencies, and consequently also by the number of the electric charges. (For more details see Chapter V.)

The positive charge on a hydrogen ion can be calculated approximately by considering that 1 mgm. of hydrogen is separated by 96,465 coulombs, and by making the assumption, which is based on definite facts, that this quantity

[redacted]

CHAPTER III.

HITTORF'S TRANSPORT-NUMBERS.

WHEN a current which is not very strong passes through a solution of copper sulphate, for a long time, between copper electrodes placed vertically, no further change seems to take place beyond the travelling of the copper with the positive current from the anode to the kathode; the anode loses as much copper as the kathode gains. Nevertheless, if the electrodes are connected with a galvanometer after the passage of the current, a polarisation-current is observed in the direction opposite to that of the primary current. Now the polarisation-current cannot be caused by gases, as in the case of the electrolysis of dilute sulphuric acid between platinum electrodes, for gases do not appear on these electrodes if the primary current is made sufficiently weak. The primary current must, therefore, have caused changes of some kind in the copper sulphate solution itself which give rise to the polarisation-current. It was soon discovered that the changes in the copper sulphate solution consisted in an increase of the concentration of the solution at the anode and a decrease at the kathode, while the total quantity of copper sulphate in the solution remained constant.

In the years 1853-59 Hittorf made a study of a great many cases of those changes which occur in the concentration of electrolytes at the electrodes. Hittorf's papers *Über d*

before electrolysis	·6765 gram CuO	
after "	·5118 "	"
it lost, therefore ..	·1647 gram CuO	= ·1315 gram Cu.

Measurements made with a silver voltameter, which was included in the circuit, showed that ·2043 gram Cu was deposited on the kathode during the electrolysis. Therefore, ·2043 − ·1315 = ·0728 gram Cu wandered from the space around the anode to that around the kathode. If 1 gram of Cu had been deposited, ·356 gram Cu would have been transported upwards. Hittorf calls ·356 the *transport-number* of copper. As 96 parts by weight of SO_4 are present in copper sulphate for 63·44 parts by weight (an atomic weight) of copper, it follows, that for 100 parts by weight of copper deposited there was available, around the kathode, $96 \times 100/63{\cdot}44$ parts by weight of SO_4. The 35·6 parts by weight of copper which wandered upwards correspond with $96 \times 35{\cdot}6/63{\cdot}44$ parts by weight of SO_4. Hence, in the time taken for the transport upwards of 35·6 parts by weight of copper, there must pass downwards

$$\frac{96}{63{\cdot}44}(100 - 35{\cdot}6) = \frac{96}{63{\cdot}44} \times 64{\cdot}4 \text{ parts}$$

by weight of SO_4. Now, 35·6 parts by weight of copper represent $35{\cdot}6/63{\cdot}44$ Cu ions; and $96 \times 64{\cdot}4/63{\cdot}44$ parts by weight of SO_4 represent $64{\cdot}4/63{\cdot}44$ SO_4 ions. Hence the numbers of Cu and SO_4 ions wandering in different directions are in the ratio 35·6 to 64·4. The movement of the ions in unit volume of the electrolyte is such that while the Cu ion wanders to the kathode, two SO_4 ions move to the anode. The value of the *transport-number* of the SO_4 ion is ·644.

The changes of concentration calculated from the data in one of Hittorf's experiments are represented by the device i

[illegible] SO_4 from above downwards. Six [illegible] at the kathode, 2 Cu ions move

upwards, while the 4 remaining free SO_4 ions move downwards, so that there are, in all, 6 free SO_4 ions under the line, and these are provided with Cu ions at the cost of the anode. It may be said that a Cu ion will pass over two of six spaces, and a SO_4 will pass over four in the same time. The quotients $\frac{2}{6}=0{\cdot}33$ and $\frac{4}{6}=0{\cdot}66$ are called by Hittorf the *transport-numbers* (*die Überführungszahlen*) for the kation Cu and the anion SO_4, respectively. These numbers express the quantities of both ions transported for each copper atom that is separated; or they may be taken to represent the distance passed over by one ion, divided by the sum of the distances traversed by both ions.

If the transport-number of the anions is expressed by n, that of the kations is $1-n$. The ratio $(1-n):n$ must evidently be the ratio of the velocities, u and v, of the kations and anions under the influence of the difference of potential at the electrodes. Consequently the equation holds good

$$\frac{1-n}{n}=\frac{u}{v}.$$

Hittorf's researches have shown the ratio u/v to be independent of the differences of potential at the electrodes, and also, within certain limits, independent of the concentrations of the solutions. The effect of temperature has shown itself to be inappreciable, if the experiments are made at about ordinary temperatures. But at higher temperatures the difference between u and v decreases more and more.

ment is represented diagram-

matically in figure 20. G is an accumulator which works the induction-machine J; $A\,B\,C\,D$ represents the branching of the current, and a, b, and c are Siemens' rheostats. The resistances in a and b remain constant; they may bear the relation to one another of 1 to 100. Z represents the cell that is filled with the electrolyte whose resistance is to be measured. If the resistance in c is now altered until the telephone, which is included in the branch $C\,D$, sounds, then the resistance in Z must be 100 times that in c.

The resistance of an electrolytic liquid is generally expressed in mercury units, one of which is equal to 0·94 ohm: the specific resistance, s, is found by taking into consideration the dimensions of the cell; s expresses the number of resistance-units of a thread of the liquid 1 metre long and 1 sq. mm. cross-section compared with an equal thread of mercury. The *specific conductivity* of the liquid, $L=1/s$, is found from s.

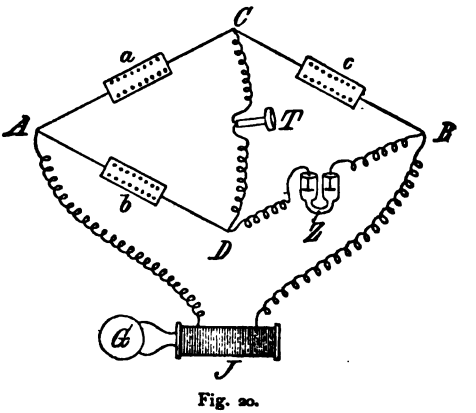


Fig. 20.

The conductivities of electrolytic solutions are much smaller than those of metals. The following table (*Table II.*) up from the results of Kohlrausch and Grotrian. and used as electrolyte is stated in column 1; the ntents of the solution (p) are given in column ives the resistance (r) of one c.c. of the solution 8°; column 4 shows the conductivity at 18° (l) at of mercury = 10,000,000; and in column 5

are given the increases of conductivity ΔL, per degree temperature, in percentages of L.

TABLE II.

Electrolyte.	p.	κ.	L.	$\frac{\Delta L}{L}$
H_2SO_4	5	4·8	305	1·21
"	30	17·4	361	1·92
HCl	5	23·5	304	1·59
"	10	17·0	340	1·57
"	20	17·3	355	1·55
"	30	17·5	370	1·53
NaCl	5	15·0	93	2·20
"	10	8·3	113	2·10
"	15	6·1	133	2·10
"	25	4·7	200	2·30
NaOH	17	3·9	320	—
$CuSO_4$	5	53·3	18	2·20
"	10	31·4	30	2·20

Mercury	0·0000943	10.000.000
Copper	0·0000017	550.000.000

Now, just as in the case of Faraday's law, so in the present case, it was [illegible] be supposed that a law to express the [illegible] different electrolytes could be arrived at [illegible] concentrations of the solutions were stated [illegible] grams; Kohlrausch, therefore, referred the [illegible] equimolecular solutions, and so obtained *molecular conductivities*. An example will make the [illegible] molecular [illegible] tivity more intelligible. The [illegible] c.c., *i.e.* [illegible] tion of potassium chloride [illegible] grams [illegible] in 100 c.c. was found to be [illegible] mercury [illegible] 0°. Hence $L = 62{\cdot}4 \times 10^{-7}$. [illegible] [illegible] oride are contained in 100 c.c. [illegible] molecule, that is 74·5 grams [illegible] tained in 1490 c.c. of an equally [illegible] follows from the value found for

L that the conductivity of one c.c. of the solution is $62{\cdot}4 \times 10^{-3}$; hence

$$\lambda = 62{\cdot}4 \times 1490 \times 10^{-3} = 93.$$

If, then, 1490 c.c. of the solution were contained in a cell between two electrodes of 1490 sq. centims. surface and placed one centim. apart, the resistance would be $\frac{1}{93}$ of a mercury unit.

The molecular conductivity of a solution of potassium chloride containing one gram-molecule of the salt in 1·49 litres is written in this form—

$$\lambda_{1\cdot49} = 93.$$

If V is taken as a general symbol for the number of litres wherein one gram-molecule of the electrolyte is dissolved, then

$$\lambda_V = L.\ V.\ 10^7.$$

Kohlrausch's results give the following numbers for solutions of potassium chloride of different concentrations, at 18° :—

TABLE III.

74·5 gram KCl dissolved in	s.	L.	λ.
0·33 litre	$0{\cdot}00399 \times 10^7$	$250{\cdot}0 \times 10^{-7}$	82·7
1 „	$0{\cdot}01088 \times 10^7$	$91{\cdot}9 \times 10^{-7}$	91·9
2 litres	$0{\cdot}02087 \times 10^7$	$47{\cdot}9 \times 10^{-7}$	95·8
	$0{\cdot}09360 \times 10^7$	$10{\cdot}5 \times 10^{-7}$	104·7
	$0{\cdot}87184 \times 10^7$	$1{\cdot}15 \times 10^{-7}$	114·7
	$8{\cdot}38223 \times 10^7$	$0{\cdot}119 \times 10^{-7}$	119·8

ers show that the specific conductivity of an ases as concentration decreases, but that the s not decrease as rapidly as the concentra- ce, the value for L_{10} is more than a ten

If the tenth part of a thin column of

[redacted]

[redacted]

[redacted]

λ for very dilute solutions of KCl and NaCl with the values for very dilute solutions of KNO_3 and $NaNO_3$], Kohlrausch found that the change of kation was accompanied by an almost constant change in the value of λ independently of the nature of the anion. An example, considered below, will make the statement clearer. Kohlrausch concluded that *the maximum molecular conductivity*, λ_∞, *of an electrolyte is made up, additively, of two constants which can only represent the migration-velocities*, u *and* v, *of the ions*. On this hypothesis he set forth the equation

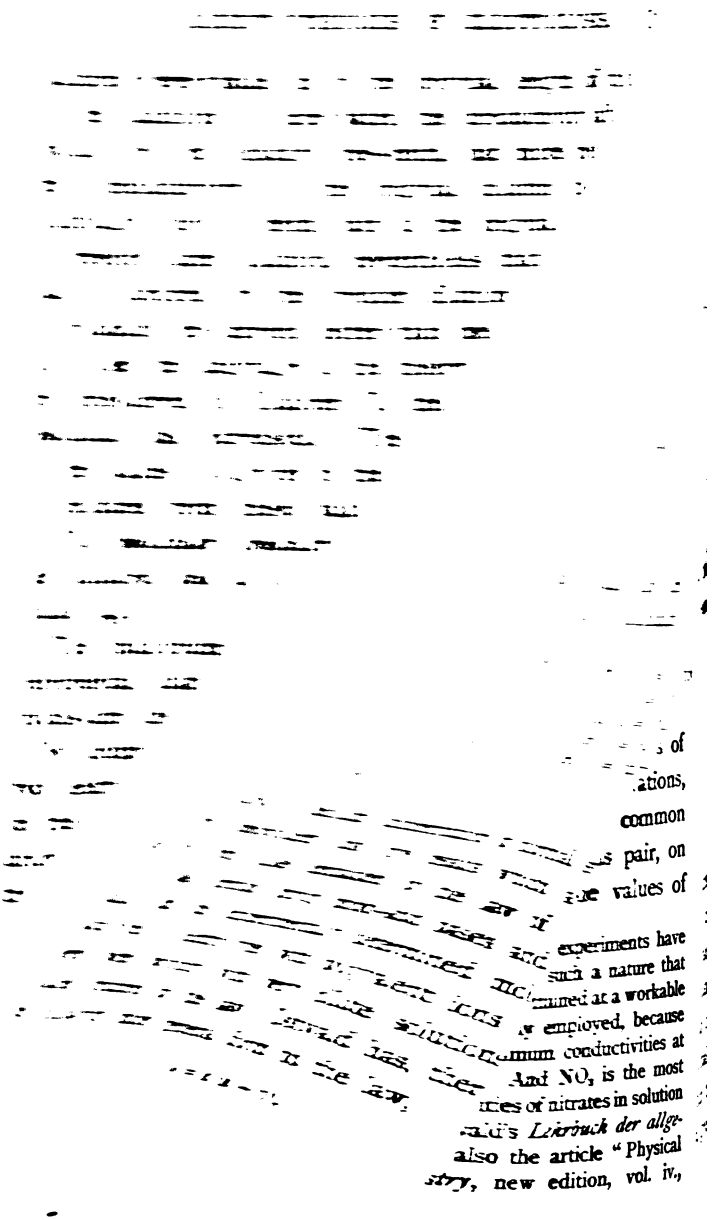
$$\lambda_\infty = u + v.$$

The values of u and v can be calculated easily; for $u : v = 1 - n : n$, where n is the transport-number of Hittorf for the anion (*see* p. 47). For potassium chloride, for example, at 25°, λ_∞, $= u + v = 140$; and, as $u : v = 0{\cdot}491 : 0{\cdot}509$, we get $u_K = 68{\cdot}6$, and $v_{Cl} = 71{\cdot}4$.

In Table IV., column I. gives the formulæ of certain electrolytes, column II. gives the values of Hittorf's transport-numbers for the kations of those electrolytes, column III. contains the most recently determined values of λ_∞ (Ostwald's *Lehrbuch der allgemeinen Chemie*, vol. ii., p. 675 of Part I.), and columns IV. and V. contain the values of u and v calculated in the way just described for the case of potassium chloride.

TABLE IV.

I. Electrolyte.	II. $1 - n$.	III. λ_∞ at 25°.	IV. u at 25°.	V. v at 25°.
KCl	0·491	140·0	68·6	71·4
$\cdot IO_3$	0·503	135·7	68·3	67·4
$\cdot Cl$	0·380	120·0	45·6	74·4
$\cdot NaNO_3$	0·387	113·7	44·0	69·7
$gClO_3$	0·499	117·2	58·5	58·7
gNO_3	0·477	124·2	59·2	65·0



...ion. The experimental ...re very meagre as yet) ... became smaller as the ...ted that *a* would become ...lution. But the degree of ...tain limit if actual measure- ...uch cases the value of *u* must ... value of λ_∞, as can be done ...e or nitrate of the kation in ... *v* must be obtained from deter- ... means of the sodium or potassium ...rned.

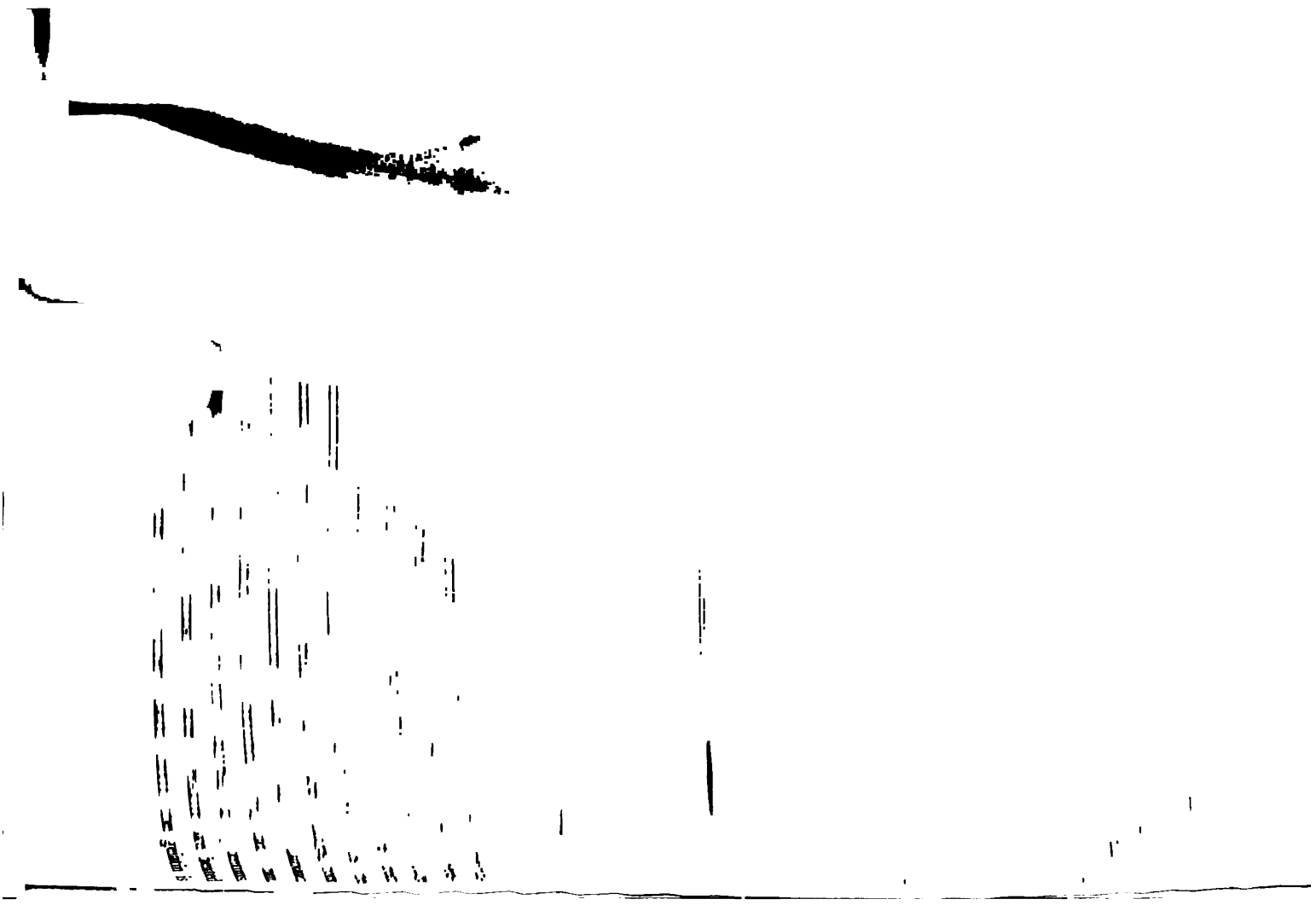
... in *Table II.* (p. 52) show that λ must ... of temperature. The following results ... a $\frac{1}{50}$ normal solution of potassium chloride: ..., $\lambda = 129{\cdot}7$ at 25°. Hence, by the equation ... Kohlrausch,

$$\lambda_{25°} = \lambda_{18°}[1 + \beta(t - 18)],$$

...mperature-coefficient is $\beta = 0{\cdot}022282$. In most ... λ increases by about 2·5 per cent. for each 1° of ...rature-increase, when working with very dilute ...ons.

...re details concerning the connections between the ...ties of ions and chemical constitution will be found ...twald's *Lehrbuch der allgemeinen Chemie*, vol. ii., Part ... 93).

...re are two experiments which, although not quite free ...ction, may be used to illustrate the law of Kohlrausch ...nt. A U-tube with platinum electrodes (*see* ... is used as the decomposition-cell in the first ... the current is passed through equimolecul... ...o sodium salts, the velocities of the anio...



dissolved; 7 grams of pure sodium chloride, and a few drops of a slightly alkaline solution of phenolphthalein, are then added, and the whole is thoroughy mixed and filtered through paper, and the rose-pink filtrate is poured into the tube *r*, where it soon solidifies. One end of the tube *r* is passed through a cork, which also carries a stoppered funnel, *t*, and a little piece of glass rod, *s*; this cork fits into the upper end of the tube *R*, the lower end of which is also closed by a cork that carries the platinum plate *k*, which serves as the kathode. By means of the stoppered funnel *t*, and the glass rod *s*, it is not difficult to fill the tube *R* with a solution of cupric chloride (1 : 10) so completely that all the air is driven out of this tube; if any air were left in *R*, some of the gelatin would be forced out of *r* when the current began to pass. The other end of the tube *r* dips into a glass cylinder, *C*, which is filled with diluted hydrochloric acid, wherein is placed a rod of gas carbon, *a*, that serves as the anode. The object of the whole arrangement is to show that, when the current passes, the hydrogen forces its way from *C*, and the chlorine from *R*, into the tube *r*, and that this is rendered visible by the decolouration of the gelatin. It is necessary, however, to leave the apparatus at rest for at least twenty-five hours before the battery is connected; for the liquids in *R* and *C* gradually diffuse into the tube *r*, with the result that the gelatin is decolourised at the end near *C* by the neutralisation of the alkali by the hydrochloric acid, and that the pink colour is replaced in the part of the tube near *R* by a slightly blue turbidity due to copper hydroxide, which is formed by the reaction between the copper chloride that diffuses into the gelatin and the caustic soda that it meets there ($CuCl_2 + 2NaOH = CuO_2H_2 + 2NaCl$).

The following numbers show the distances passed over in

[redacted]

iat remain over combine with the chlorine ions that
. from the kathode, and so produce a neutral salt.
comes about that, as the ions travel through the
the alkali is removed at both sides, and the phenol-
in becomes colourless.

lecolouration of the gelatin would have been accom-
by the diffusion process alone, in
ie during which the current has been
. to pass, to the distance of 0·9 centim.
the anode and 0·4 centim. from the
de; these numbers must therefore be
ted from 18·8 and 3·7 respectively; the
nces, 17·9 and 3·3 centims., express
atio of the velocities of migration of the
H and Cl under the influence of the
ent.

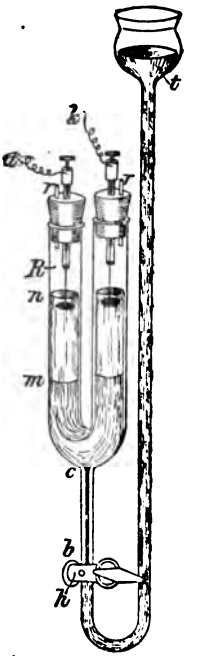
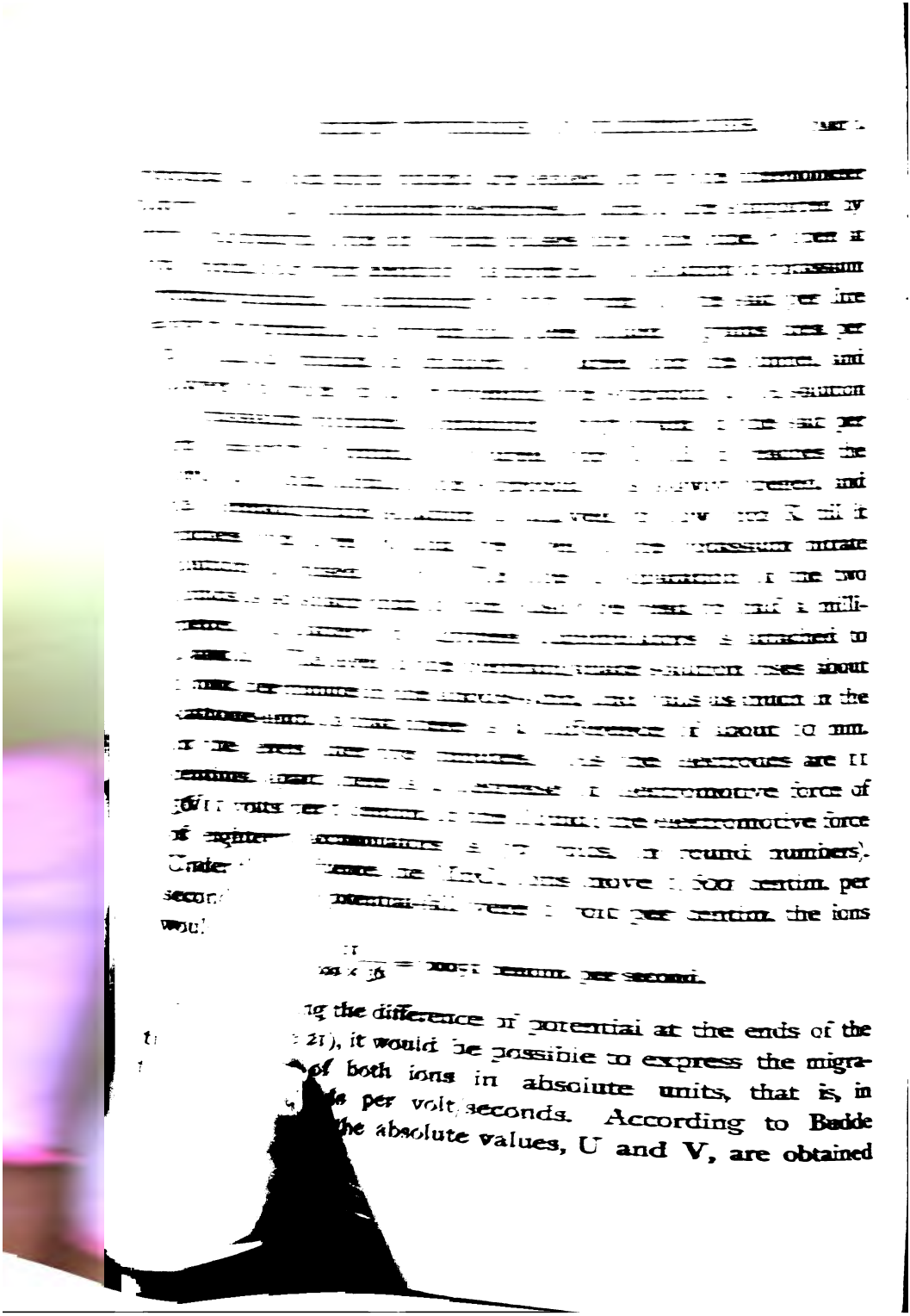


Fig. 22.

ne experiment shows that the hydrogen
advance towards the kathode about five
es more quickly than the chlorine ions
ve towards the anode. Graham's experi-
nts proved that a salt diffuses through a
y at a rate scarcely less than that at
ich it diffuses through pure water; hence
may conclude that the numerical results
the present experiment would not be
tered by substituting water for gelatin.

N *it[s] hrift für Elektrochemie* **3**, 308 [1897]) has
instructive, and easily conducted, experi-
ɔrating the migration-velocity of the violet
mall U-tube (R figure 22), whose limbs are
ıd 12 mm. wide, is furnished with a milli-
s fused to a piece of thermometer tubir
4 centims. long and 1 mm. wide. T



ng the difference of potential at the ends of the
21), it would be possible to express the migra-
of both ions in absolute units, that is, in
e per volt seconds. According to Badde
he absolute values, U and V, are obtained

by multiplying the relative quantities u and v by the factor 110×10^{-7}; these values are thus obtained :—

$$U_H = 0{\cdot}00352 \text{ and } V_{Cl} = 0{\cdot}00069 \text{ centim. at } 18°.$$

That is to say, the ions travel 0·00352 and 0·00069 centim. respectively, in one second, provided the difference of potential at the ends of the tube 40 centims. long is exactly 40 volts.

The following values are given by Kohlrausch (*Wied. Annal.*, **50**, p. 403) for very dilute solutions :—

U_H	= 0·00352 centim.	V_{NO_3}	= 0·00063 centim.
U_K	= 0·00066 „	V_{Cl}	= 0·00069 „
U_{Na}	= 0·00045 „	V_{ClO_3}	= 0·00057 „
U_{Ag}	= 0·00057 „	V_{OH}	= 0·00181 „

The migration-velocities of polyvalent ions have not been determined as yet with sufficient accuracy.

CHAPTER V.

THE DISSOCIATION THEORY OF ARRHENIUS.

IN 1887 Svante Arrhenius put forward his *theory of the dissociation* [illegible] and thereby gave an explanation which might be accepted of those phenomena of electrolytic conductivity which had been summed up by Ostwald in the general formula $\lambda = x\,\lambda - \lambda'$.

As the law of Kohlrausch tells that under the influence of the electric current the ions travel with definite velocities dependent on their chemical natures, and as it must be a matter of indifference which anion belongs to a determinate kation, Arrhenius asserted that *the molecules of electrolytes in aq[illegible]ns are already dissociated into their two ions [illegible]ded with their respective electric charges*: that [illegible]es not, therefore, require the previous splitting [illegible]le by the electric current. While under ordinary [illegible]e ion [illegible] irregularly to and fro among the [illegible]ules, [illegible]ion will sometimes approach and rece[illegible]n ion of the opposite kind, if a [illegible]of po[illegible]stablished between the electrodes in t[illegible], then, according to Arrhenius, the [illegible]d[illegible] the kation goes toward the kathode [illegible]he anode, and they also move more [illegible] which the electrolysing current has [illegible] frictional resistances experienced by

the ions from the water molecules which stand in their way. These resistances vary in accordance with the nature of the ions, and the greater they are the smaller is the mobility of the ions, and therefore the smaller their migration-velocities. These electrolytic frictions are very considerable, according to Kohlrausch (*Wied. Annal.* **50**, p. 407). To drive forward a gram-ion, in dilute solution, with a velocity of 1 centim. per second, requires a force equal to the weight of 984,000/(E. U) or 984,000 / (E. V) kilograms, where E. is the equivalent weight of the ion, and U, or V, is the velocity of migration of the kation, or anion, in absolute units (see end of last chapter). For 39·1 grams potassium, in dilute solution, would be required a weight of 984,000 / (39·1 × ·00066) = 38×10^6 kilograms. This very considerable quantity of work, which is used for the transport of the ions, and which forms a substantial part of the energy that is brought into the solution by the current, is transformed into heat; just as a portion of the current-energy, depending on the specific resistance of the conductor, is changed into heat in a metallic conductor.

But if the current is to pass continuously through an electrolyte it must perform a second portion of work at the ectrodes; it must neutralise the ions that are attracted the electrodes, either by drawing away the charges that to them with a definite intensity, or by forming new fr terial of the electrodes or from the water, kations and new kations for the anions.

assage of a current through an electrolytic
n the presence of free ions in the liquid,
[non-ionised] *molecules that may be in*
in the carrying of the current.

$a(n+v)$, the factor a expresses what
ical value λ_∞ the experimentally
tually is. But in the dissociation

[illegible]

[illegible] chemically pure liquids is undoubtedly hydrogen [illegible] or [illegible] pure sulphuric acid do not conduct, [illegible]se, according to the dissociation theory, their molecules [illegible]ot ionised; for the same reason chemically pure [illegible] is [illegible]ectrolyte; for the water purified by [illegible]

[illegible] seems [illegible]er to use the terms *ionisation*, and *ionisation-*[illegible]*ent*, ra[illegible]sociation, and dissociation-coefficient. Dis-[illegible]ion h[illegible] thought of as a process of separation of [illegible]ules atomic groups, such that the products are [illegible]nect[illegible]al bonds and can be separated from one [illegible]er

Kohlrausch and Heydweiller, and distilled in a vacuum, showed a specific resistance at 18° of $24{\cdot}75 \times 10^{10}$ mercury units (*Sitzungsberichte der K. preuss. Akad. physic.-math. Klasse*, 1894, p. 295). A column of that water 1 mm. long would oppose a somewhat greater resistance to the passage of a current than that of a copper wire of equal thickness stretched three hundred times round the equator. The molecular conductivity of a litre of that water would be $0{\cdot}404 \times 10^{-4}$; and, as $u_H = 290$ and $v_{OH} = 165$, the dissociation of the water would be so small that 1 gram H ions and 17 grams OH ions would be contained in $12\frac{1}{2}$ million litres.

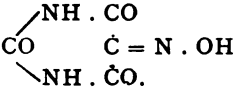
Water as pure as this may, therefore, be regarded as a non-conductor; and it may be taken for granted that the water in a solution does not take a primary part in the electrolysis of the solution.

The circumstance that the most carefully distilled water is not a perfect non-conductor is due, according to the accurate observations of Warburg (*Wied. Annal.*, 1895, p. 396), to the presence of very minute quantities of impurities which are electrolytes, and which are extremely difficult to remove. The very small conductivities which are always found to be exhibited by such organic compounds as aniline, xylene, and turpentine-oil, however carefully the compounds [illegible] purified, are to be assigned to a similar cause. [illegible] recommends the removal of impurities of this kind [illegible]sis, a process whereby the compounds are *purified*

[illegible]he facts that neither any simple electrolyte, nor [illegible]nducts the current, it is extremely remarkable [illegible]solutions of these electrolytes should allow [illegible]pass. The water must be looked on as abl[illegible] molecule of an electrolyte into its two ion[illegible]

[illegible]

There are certain aniline colouring-matters which behave towards water and towards other solvents similarly to hydrogen chloride. A very little [of the potassium salt of] *eosin*, $(C_{20}H_6Br_4O_5)K_2$, is shaken with a mixture of 20 c.c. ether and 1 c.c. alcohol, and the liquid is poured through a filter of the best Swedish paper. The filtrate is perfectly colourless, although it contains traces of a salt of potassium in solution. If a couple of c.c. of water are now added, and the liquid is shaken, the watery solution that settles to the bottom of the vessel looks rose-red by transmitted light, and shows a beautiful green fluorescence in reflected light. This production of colour is obviously to be referred to the ionisation of the saline compound of eosin by the water. The research of E. Buckingham (*Zeitschrift für physikal. Chemie*, **14**, pp. 129-48 [1894]) shows that the fluorescence is certainly due to the complex anion of the eosin salt, for the fluorescence is the stronger the more the ionisation is promoted. *Methylene blue* ($[C_{16}H_{18}N_3S]Cl$), which is the chloride of a complicated kation, may be used to demonstrate, by a change of colour, the ionising action of water. The compound dissolves very slightly in the mixture of alcohol and ether mentioned as above, without colouring the solvent ; but as soon as the solution is shaken with water, the compound is ionised, and the free kations $H_{18}N_3S$) which are now present give to the water a blue colour, as intense as that of a saturated solution per sulphate. Violuric acid is also a suitable substance cognising the dissociating action of water. This acid constitution



epared by heating a solution, as concentrated

ned, indirectly, from the change that occurs in the
tween the copper electrode and a solution of copper
erature changes.

the algebraic sum of two quantities—namely, the heat of ionisation, j, of copper, and that quantity of heat which is equivalent to the electrical energy, E, corresponding with the difference of potential, π, between the copper electrode and the (normal) solution of copper sulphate. Now as $\pi = +0{\cdot}6$ volt, according to measurements (carried out with a capillary electrometer) wherein the potential of the electrolyte = 0, and hence is smaller than the potential of the electrode, the quantity of energy set free, E, when one gram-atom of copper dissolves, is

$$\begin{aligned} E &= 2 \times 96{,}500 \times 0{\cdot}6 \text{ volt-coulombs} \\ &= 27{,}700 \text{ gram-calories.} \end{aligned}$$

Hence, as the equation $w = E + j$ must hold good, it follows that

$$\begin{aligned} j &= 10{,}200 - 27{,}700 \\ &= -17{,}500 \text{ gram-calories.} \end{aligned}$$

This result means that 17,500 gram-calories disappear during the process of ionising one gram-atom of copper; so that the ion of copper is richer in energy, by this amount, than the gram-atom of copper.

It is very easy to deduce the value of j for zinc from the value for copper. The thermo-chemical equation,

$+ CuSO_4 Aq = ZnSO_4 Aq + Cu + 50{,}100$ calories, tells

50,100 calories are given out when one gram-ion of
is un-ionised and at the same time one gram-atom
is ionised. Now as 17,500 calories must be set free
passage of one Cu ion into the non-ionised state,
ess of ionising one gram-atom of zinc must produce
17,500 = 32,600 calories. Hence, one gram-ion
orer in energy, by this amount, than one gram-at
metallic zinc.

ine numbers must be accepted as quite
e it is ... ...s in determining the values
... the ... = 2 — Ī ; see p. 71), never-
... w ... ...ss of ionising an atom is
...me... ...gun. and sometimes by a
... ...lements which show greater
...y a... ... energy in the ionic state,
...y ha... ...d from without to the less
...ive ... order to ionise their atoms.
...e ... of the ions of the former

elements can be accomplished only by the expenditure of much energy, whereas the ions of the latter elements readily separate from their solutions. [All the metals which are easily ionised show positive heats of ionisation; the others show negative heats of ionisation.]*

Especial stress should be laid on the fact that the process of ionisation does not necessarily involve a consumption of energy; all that can be said in general terms is that *the energy inherent in the atoms undergoes a transformation during the process of ionisation.* While a portion is changed into electrical energy, another portion may pass out of the system; or energy may be taken up from without, whether in the form of heat, or in the form of light-energy, both of which forms are changed into electrical energy during processes of ionisation. The total quantity of energy in an element when it is ionised is greater or less than before ionisation in accordance with the general chemical character of the element.

It was not at first easy for the new theory of electrolytic dissociation to hold its ground, and although the number of its adherents has increased very rapidly, thanks to the assiduous labours of its champions, there are still both
ts and chemists who cannot see their way to accept
ence of free portions of molecules carrying electric

ph the most part, regard the way of
f sing current from the point of view
! rotthuss, which dates from the year
esented the work of the current as
ıg of the molecules in rows, and
ns, at the electrodes, from this

ıtence from Ostwald's paper referred to

[illegible] that this [illegible] and its transformation [illegible] as by Clausius [illegible], Part VI.) [illegible] that if the hypothesis were correct, a current of an ampère would not act as a conductor [illegible] ampère) had become sufficient to effect the decomposition of the molecules [illegible] would be marked by the sudden deviation [illegible] included in the circuit [illegible] decomposed all at once. In a current of the minimum number of amperes sufficient to maintain electrolysis, provided the electrodes consist of the same metal as the kation of the electrolyte, and provided the tension that prevails at the electrodes is just sufficient to overcome the electromotive force acting in the opposite direction, which force is generally small, and is dependent both on the material of the electrodes and on the character of the ions which give up their charges more or less readily. When these conditions are fulfilled, the needle of the galvanometer begins to move. The deviation increases quite gradually as the electromotive force of the current increases, and as, in consequence, the quantity of current passing through the solution increases, the quantities of the ions that are separated also become greater in accordance with the law of Faraday. Experience shows that electrolytes of the second class obey Ohm's law absolutely. This could not be the case if the hypothesis of Grotthuss were accepted [without any modifications or additions].

the current were really employed in of the electrolyte, then those electro- ld together by weak affinities, in the

chemical sense of that term, are just the electrolytes which ought to exhibit large conductivities. Experience goes against this conclusion also; for a solution of mercuric chloride conducts much worse (because of the smaller ionisation) than a solution of potassium chloride, and when potassium-silver cyanide is electrolysed, the potassium, which must be more firmly held than the silver, goes to the kathode, while the silver travels with the cyanogen to the anode. The ionisation theory is free from those objections which apply to the older theory; it takes the facts of electrolysis into account in a complete way, as has appeared from the examination of the theory made in preceding paragraphs.

Those chemists who deny the existence of free ions, because the chemical behaviours of these ions are said to be different from the behaviour of the neutral atoms, are to be reminded that *the quantities of energy associated with the ions are different from the quantities that are associated with the free elements, and that the ions must, therefore, differ qualitatively from the free elements.*

That the $K^{\cdot}$ in a solution of potassium chloride does not react with the water, that hydrogen is not given off from this solution, and that the Cl^{1} is odourless, depend either on the chemical energies of the ions being different in degree from the chemical energies of the free elements, or on the stoppage, by the electrical charges on the atoms, the exhibition of the ordinary chemical effects of the gies of these atoms. Zinc dissolves in hydrochloric but when it is charged negatively it does not ve. It is customary to explain the different degrees diness to enter into reaction that are shown by ic forms of such elements as phosphorus, oxygen, bon, by the supposition, which is well grounded, o

[illegible] Part I

[illegible] different arrangement from that

[illegible] the [illegible] the [illegible] the [

once made manifest by the ionisation theory. For the minute particles exchange ion for ion, and this the more quickly the greater is the mobility of the ions, and the more completely the ionisation has advanced. The dissociation-coefficient of Ostwald, α [*see* p. 66, where it is proposed to call α the *ionisation-coefficient*], gains a wider meaning as it becomes also the coefficient of activity in chemical reactions, and it will perhaps point the way by which measurements of chemical affinity may be made.

If the saponification of ethereal salts proceeds at the same rate whatever base or acid be used, provided only that the degrees of ionisation of the acids or bases employed are the same, this supposes the presence of free OH', or free H', and therefore an ionisation of the molecules of the base, or of the acid. This process of saponification is carried on at the same rate by solutions of all bases and acids of equal molecular concentration, provided that $\alpha = 1$, just as all very much diluted solutions of acids, containing the same number of gram-molecules, invert cane-sugar at the same rate.

It is evident that the reagents which serve to detect an element when that element is in the ionic condition, will no longer be serviceable when the element in question has combined with others to form a compound ion. For instance, in the ClO_3' ion of potassium chlorate cannot be solution of a silver salt. Further, the facts that on in the potassium salts of ferro- and ferri- not precipitated by ammonium sulphide, and ot precipitated from solutions of its salts by n tartaric acid is present, find a reasonable e statement that the conditions of normal fulfilled in these cases, because the metals

[illegible] ions, but are [illegible] mentioned [illegible] larger limitation [illegible] and [illegible] double [illegible] ; whereas [illegible] the rest of the [illegible]

[illegible] that both the [illegible] solutions of salts [illegible] reagents are mixed for [illegible], and also [illegible] the years of neutralisation [illegible] strong bases, are [illegible] theory. The quantity of heat set [illegible] neutralisation of a strong acid in solution by a strong base used in solution to form a salt which remains [illegible] according to the theory, to the combination of the H ions of the acid with the OH ions of the base, and must therefore be independent both of the [illegible] of the acid and of the metal of the base; moreover, [illegible] have the same value.

[illegible] for a monobasic acid,

[illegible] change [illegible] occur in consequence of [illegible] Arrhenius, *Zeit. für physik.* [illegible] pare Ostwald's article, "Elec- [illegible] *Dictionary of Chemistry*, new [illegible] iv., p. [illegible]]

[illegible] of [illegible] as found acceptance in physio- [illegible] servations made by Paul and [illegible] *Chemie*, **21**, p. 414 [1897]), that

the poisonous actions of metallic salts are connected with the degrees of ionisation of these salts, are interesting. Alcoholic solutions of corrosive sublimate and silver nitrate have no effect on the bacilli of anthrax. It has long been known that potassium ferrocyanide is not poisonous; the ionisation theory gives an explanation of this fact. There are other metals which are poisonous when present as kations ($Cu^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Ag^{\cdot}$), but become less poisonous, or non-poisonous, when they form parts of complex anions (even when combined with cyanogen). The disinfecting action of potassium-silver cyanide is much less than that of silver nitrate, and a dilute solution of Fehling's reagent is without harmful effect on plant-seeds.

Ostwald (*Zeit. für physik. Chemie*, **2**, p. 271, and **3**, p. 120 [1888-89]) has described experiments intended to furnish direct evidence of the existence of free ions; but only one of the experiments appears to me to be capable of being readily performed, by the arrangement which is described in the following paragraph.

A glass tube, 40 centims. long and 1 centim. diameter (*RR*, figure 23) is bent at right angles near the ends, and two pieces of tubing, each about the size of a test-tube, are fused it, as shown in the figure. One of these tubes is tightly by a good cork, through which passes a rod of very ıalgamated zinc, *a*. A piece of platinum, *k*, is fused th of the other tube near the bend; the u th diluted sulphuric acid, and a cork i this tube, which cork carries a narrow right angles, and containing coloured w tube serves as a manometer. If connected with the positive pole, with the negative pole, of a batter drogen instantly appears on th

in the neighbourhood of

the platinum, and these must have escaped as gas after their electrical charges had been neutralised.*

The ionisation theory seems, then, not only to be vindicated against all objections, but it is demanded for the explanation of diverse processes. The justness of the theory is exhibited yet more significantly by phenomena which belong to a domain that is somewhat removed from that of electrolysis, and which will be considered in the next part of this book.

* This experiment is explained by supposing the occurrence of a frequent exchange of ions between the molecules of the electrolyte. If such exchanges occur, there must probably be periods whereat the slightest directive force will suffice to precipitate the ions, that are for the moment nearly free, on to the electrodes. (Compare Lodge's *Modern Views of Electricity*, pp. 72-87; and Fitzgerald's "Helmholtz Memorial Lecture," in *Chem. Soc. Journal*, **69**, p. 885 [July, 1896]). —[TR.]

VAN'T HOFF.

[illegible] van't Hoff [illegible] theory [illegible] has opened extra- [illegible] it has been [illegible] the affinities of [illegible] possible to bind [illegible] foundation, a [illegible] before be brought [illegible] great service [illegible] as it has called [illegible] methods for determining [illegible]

[illegible] attended to in this part [illegible] van't Hoff's theory and the [illegible] electrolytic dissociation—for that subject has been [illegible]—and the elucidation of the con- [illegible] As the theory of van't Hoff is [illegible] Arrhenius's theory of the origin of the [illegible] which [illegible] considered in the last part of this book, [illegible] somewhat fully into the work of van't [illegible] seem at first sight as if we were [illegible] at have nothing to do with electro- [illegible].

CHAPTER I.

OSMOTIC PRESSURE

WHEN a substance does not react chemically on a liquid wherein it is soluble, we are accustomed to regard the process of dissolution as purely physical and the solution as a molecular mixture. The changes of volume-energy and thermal-energy which accompany the process of dissolution are positive or negative according to the state of aggregation of the substance to be dissolved, and these changes generally proceed in the same direction when a concentrated solution is diluted with the solvent. But when the dilution has reached a definite limit, these changes of energy can no longer be observed: the volume of the dissolved substance is then small compared with that of the solvent. The following considerations apply in the main to solutions whose concentrations approach that limit; although more concentrated solutions serve better for certain demonstrations, because they produce more marked effects and produce them more rapidly.

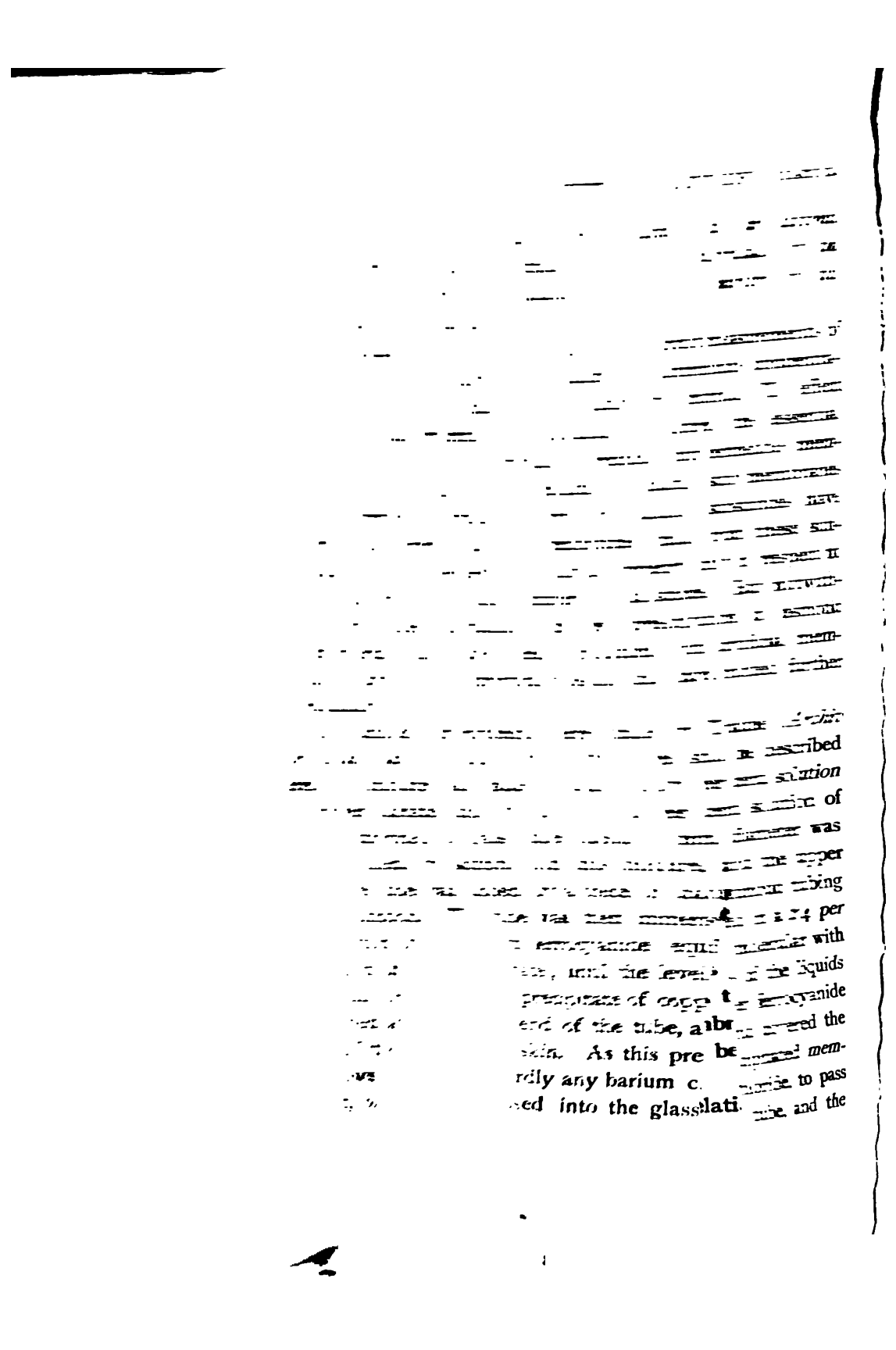
If a more dilute solution of a coloured salt—for instance, an aqueous solution of copper sulphate or potassium bichromate—is poured carefully, with the aid of a cork disc on the end of a glass rod, over a more concentrated solution of the same salt, it is observed that the concentration of the former solution gradually increases, while that of the latter decreases.

the more exact relations between

smotic pressure and concentration it is necessary to make
se of membranes which are completely *semipermeable*, that is,
hich can be passed through by the molecules of the solvent,
t not by those of the dissolved substance. This condition
ot completely fulfilled by an animal membrane; for the
ence of sugar can be detected in the water wherein the
der stood for some hours in the experiment that has
been described.* Perfectly semipermeable membranes
nown, but they are few in number.

the epidermal cells from the underside of the mid-rib of
of *Tradescantia discolor* are floated in a 10 per cent.
n of nitre, the protoplasmic contents of the cells may
n, under the microscope, to become detached from the
lls, and to contract, while the salt-solution occupies the
etween the protoplasm and the walls of the cells.
Vries, who studied osmose in plant-cells in 1884,
his phenomenon *plasmolysis*. The delicate pellicle
rrounds the protoplasmic contents of the cells acts
ipermeable membrane in this experiment. This
allows the passage of water from the contents of
ien the concentration of the salt solution is a very
er than that of the cell-sap. When de Vries had
the concentrations of those aqueous solutions of
stances which just brought about the plasmolytic
plant-cells, he found that these solutions were
, that is to say, he found that they contained
the dissolved substances proportional to the
ights of those substances. *Equimolecular solu-*

detected by boiling a small quantity of the water wherein
with a trace of dilute sulphuric acid, and then adding an
hling's solution (10 grams copper tartrate + 500 gra
s pure caustic soda), when a red precipitate of cupr



ıembrane was extended outwards, like a bubble, by
e osmotic pressure exerted by the solution of barium
loride.

Traube supposed that the semipermeability of a membrane
copper ferrocyanide is due to the membrane acting like
ieve, the meshes of which allow the smaller molecules
water to pass, but stop the larger molecules of the
lved substance. Tamann (*Zeit. für. physikal. Chemie*,
255 [1892]) has found, however, that these mem-
s are quite impermeable by solutions of the chlorides
itrates of calcium and magnesium, but only partially
neable by the chloride and nitrate of barium ; hence
nks that Traube's hypothesis is wrong. According
nann, freshly precipitated copper ferrocyanide is
ıted compound which is able to act as a solvent
certain substances ; and the molecules of all those
es which dissolve in this compound are capable
ıg through the membrane, while those substances
e *insoluble* in the compound are held back.

ır to carry out osmotic investigations on a larger
the precipitated membrane that has been described'
'l necessary to give to the membrane the proper
withstand resistance. This was done by Pfeffer
Untersuchungen, Leipzig, 1877), by forming the
ın the walls of a porous clay pot. The prepara-
membrane that is sufficiently compact and cohesive
ı attended with some difficulty. It succeeds
ler the porous pot. Pfeffer used pots 4·6
1·6 centims. diameter. He fastened a glass
as a stopper, in the neck of a pot wherein
been formed ; and to the side-piece
affixed a mercury manometer with
ıe then completely filled the appa

examine the phenomena of osmotic
tatively, a bell-shaped glass vessel of

25 c.c. capacity may be employed (*see* figure 25); the wer opening of this vessel, which is 7 centims. diameter, closed by a porous plate formed by sawing off the bottom a porous cell and filing it to the proper size; this porous ate must be fastened securely by means of sealing-wax. ter the glass vessel has stood in boiling water for an hour at it may be thoroughly saturated with water), it is filled h a 3 per cent. solution of potassium ferrocyanide, and k in a vessel which contains a 3 per cent. solution of per sulphate until the levels of the liquids equal. If the porous plate fits firmly, the vn precipitate of copper ferrocyanide will be seen either in the glass vessel or in the d outside that vessel. The membrane that oduced acquires a sufficient thickness after days. The glass vessel is now prepared, for all, for osmotic experiments; it is with a 50 per cent. solution of cane and closed with a cork through which a thermometer tube, *r*, of 1·3 mm. clear ess, furnished with a scale. A little red alkali-blue is shaken into the bore of rmometer tube before that tube is fixed lace; this powder adheres to the sides of the tube, and the rise of the sugar solution very evident by the lour which it imparts to the liquid. If the apparatus fastened by means of the cork *k*, in a vessel filled ıter, *C*, the liquid in the thermometer tube rises at age rate of 1 mm. per minute. After the experiment ed, even if it proceeds for so long as five hours, the *C* shows merely a trace of sugar when tested with solution.

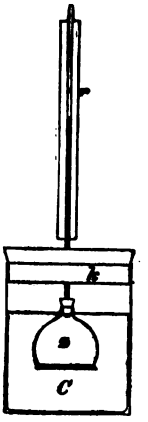


Fig. 25.

tory results are obtained by the use of a cylindrica

[illegible] the Royal Porcelain Manufactory, Berlin.

unsen burner. If the cell is now sunk over the rim
a cylinder filled with water, the indigo solution in the
anometer rises at about the rate of 10 mm. per minute,
the bore of the tube is 0·79 mm. The osmotic taking
of water proceeds about four times as quickly as in the
eceding experiment.

A Pukall's cell provided with a precipitated membrane
ems to be suitable for quantitative, as well as for qualitative,
notic experiments. When a 1 per cent. sugar solution was
ced in the cell, and the manometer was filled with mercury,
mercury rose after some weeks to a height which agreed
ely with the pressures found by Pfeffer: and not a trace
ugar could be detected in the water outside the cell.

he following experimental arrangement, recommended
ffer (*loc. cit.* p. 12), is not suited for measuring pressures,
has the advantage that experiments can be carried out
easily and quickly. A glass tube, 12 centims. long
2·5 centims. wide (*R*, figure ·26), is used in place of
s pot. The lower edge of this tube, having been
ed somewhat and ground, is brushed over with shellac,
a piece of parchment, *H*, is bound over it very firmly.
precipitated membrane is then formed in this parchment
usual way. The rest of the arrangement, which is the
as that used in the experiment with a Pukall's cell,
een described above; the glass tube *R* is finally fixed,
s of a cork, in the neck of the bottle *F*, which
ter. It should be mentioned that 0·1 per cent.
ferrocyanide is added to the sugar solution,
cent. (the equivalent quantity) of copper nitrate
for the purpose of repairing damage done to
l membrane during the experiment. The rate
quid rises in the manometer varies to so
e thickness of the precipitated membra

nploy a more profitable form of the equation in general
iemistry. As both laws hold for all ideal gases, indepen-
ntly of their chemical compositions, Avogadro, as is well
iown, made the following statement : *Equal volumes of*
gases, measured under the same conditions of temperature
d pressure, contain equal numbers of molecules. Not only has
s statement been confirmed by numberless determinations
molecular weights, but it has also been deduced directly
m thermodynamical principles. One litre of hydrogen
asured at 0° and 76 centims. mercury-pressure weighs
) gram; hence one gram-molecule, that is two grams,
iydrogen occupies 22·38 litres at normal temperature and
isure. In accordance with Avogadro's law, the normal
ime, that is to say, the volume occupied by a molecular
ht in grams, of any gas must then be 22·38 litres. Now if,
wing Horstmann, the volume v_0 in the gaseous equation
$p_0v_0T/273$ is put as the gram-molecular volume = 22·38
= 22,380 c.c., and if it is borne in mind that 76 c.c. of
ury weighs 1033·3 grams, and, moreover, if p is measured
ams and v in c.c., the equation takes the following
er form :—

$$pv = \frac{1033{\cdot}3 \times 22{,}380 \times T}{273} = 84{,}700\ T \text{ gram-centims.}$$

p is measured in atmospheres, and v in litres, the
takes this form :—

$$v = \frac{22{\cdot}38 \times T}{273} = 0{\cdot}0819\ T \text{ litre-atmospheres.}$$

-atmosphere = 1033·3 × 100 × 10 gram-centims.
" = 103·33 kilo.-decims.)

42,750 gram-centims. = 1 gram-calorie, the
s this form :—

$$v = \frac{84{,}700 \times T}{42{,}750} = 2\ T \text{ gram-cals.}$$

[redacted]

[redacted]

[redacted]

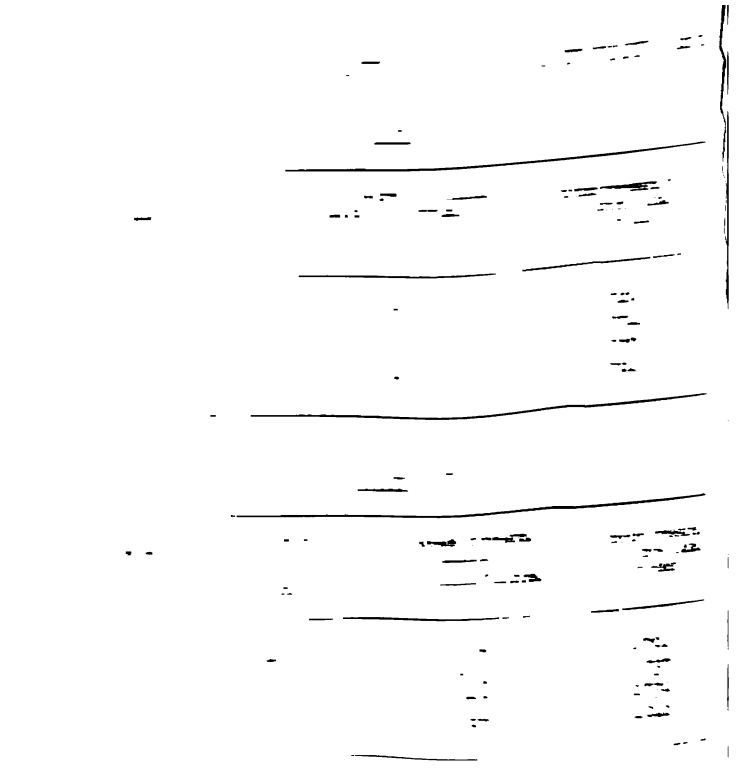
III. What amount of work is done by 1 kilo. of gen when it is heated to 100° at the atmospheric sure?

ne kilo. of oxygen contains 1000 / 32 = 31·25 gram-cules. Hence the work amounts to

84,700 × 31·25 × 100 = 264,687,500 gram-centims.
= 2646 kilogram-metres;
0·0819 × 31·25 × 100 = 256 litre-atmospheres;
2 × 31·25 × 100 = 6187 gram-calories.

gaseous equation proved of very signal service to off in his further speculations concerning osmotic An extraordinarily close relation was found between ressure, P, and the gaseous pressure, p, when the $pv = 0{\cdot}0819\ T$ litre-atmospheres was applied to esults. The osmotic pressure $P = 0{\cdot}649$ atmos. per cent. solution of cane sugar exerts at 0° van't Hoff in place of p in the above equation. grams of water containing 1 gram of sugar in upy 100·6 c.c., it follows that 1 gram-molecule as) of sugar is contained in 100·6 × 342 c.c. = a 1 per cent. solution of sugar. This volume d for v in the foregoing equation; and van't nd $R = 0{\cdot}649 \times 34{\cdot}4 / 273 = 0{\cdot}0818$ litre-atmo-is exactly the same value as that of the on.

Hoff calculated the pressure of a gas is equimolecular with that of a 1 per of cane sugar—that is, a gas containing 1 n 34·4 litres—at the temperatures whereat mined the osmotic pressures of the sugar alues of the two pressures are given in



...solu-
...ter at 15°
...measured pres-
... The agreement
... is evident; and a
... other substances besides cane
... of the osmotic pressures of
... have gone

... = 2·815 T litre-atmospheres, is,
... solutions, when the osmotic
... of the gaseous pressure, p (in
... volume, v (in litres), is sub-
... olution, V, that is, the number of
... olecule of the substance. On the

ound of this agreement, van't Hoff came to the conclusion
t the osmotic pressure is equal to the gaseous pressure
ch would be observed were the solvent removed and the
olved substance caused to occupy the same space as the
ion, at the same temperature as that of the solution.
conclusion may be stated in the following words: *The*
ules of a dissolved substance exert the same pressure
t a semipermeable membrane, during osmotic processes,
would exert against the walls of an ordinary vessel
ey in the gaseous state at the same temperature and the
ncentration.

thus extending the law of Avogadro to solutions,
asis of Pfeffer's researches, van't Hoff also confirmed
of de Vries, according to which osmotic pressure is
tioned by the quality of the molecules of the dis-
bstance, but only by the number of these molecules,
these results he associated the conclusion that
mal conditions, a substance which is not an
is separated by the process of dissolution into
cules.

getics of solutions must be analogous to those of
ce the same work must be done by the change of
nergy of a solution, measured by $P\,d\,V$, as in
equimolecular volume of gas under correspond-
of pressure and temperature. The measure-
otic pressures by Pfeffer's apparatus depends,
on this; inasmuch as the air is compressed
nb, and the mercury is raised in the open
ometer, until the opposite pressure thus
to the osmotic pressure. In the first
a shifting of the volume-energy; in
is a transformation of volume-ener
ion. A 1 per cent. sugar soluti

[illegible] the same solution in the [illegible] manometer. If the cross-section of this limb [illegible] small, the amount of work done would be [illegible] for 1 c.c. opposes a pressure to the surface of the liquid equal to 981 dynes, [illegible] millimetres of mercury. If a lateral overflow-tube [illegible] attached to the open limb at a less height than that [illegible] mentioned, liquid would flow from this tube until the solution in the cell had become so dilute, by taking up water, that equilibrium was attained between the osmotic pressure of this liquid and the hydrostatic pressure of the column of liquid in the manometer. The apparatus might thus be made to work as a machine for raising water (*see* figure 26, p. 56, where a small pail is shown on a side-tube attached to the manometer).

The effect of osmotic pressure, and, consequently, the analogy between osmotic and gaseous pressure, will be rendered clearer by imagining the following arrangement proposed by van't Hoff. In a vertically placed glass tube, open above and closed below, is placed a partition, formed of a sol[illegible]eable membrane, which fits securely into the [illegible] same time it is capable of free movement [illegible] the tube. Water occupies the space above [illegible]d a solution is placed in the space under [illegible] pressure of the water-column is greater than [illegible]sure of [illegible]ution, the partition will sink, [illegible]on will [illegible] more concentrated. But if [illegible] the [illegible]nn is less than the osmotic [illegible] partition will rise, and the [illegible]d so become more dilute. In [illegible] partition will continue until [illegible]d which is just compensated [illegible] of water.

The readiness to do work of a solution, exactly like the me quality of a volume of a gas, is the greater the more e volume is decreased, that is, the more concentrated the *ution* is made. But this work which the osmotic pressure i solution performs, if opportunity is afforded the solution ike up solvent through a semipermeable membrane, must xpended in order to restore the former degree of con- ation. And this work which is expended in the *ntration* of a solution cannot be measured directly by ic experiments, because the arrangement of van't Hoff racticable in such cases. Measurements can, however, le indirectly by the aid of the processes of boiling and ; which generally make it possible to obtain a more *estimation* of the osmotic pressure (see Chapters III. of this part).

ards the magnitude of osmotic pressure, the high ich this pressure attains even in dilute solutions are surprising. In a 5 per cent. sugar solution at 0 the *nounts* to $5 \times 0{\cdot}649 = 3{\cdot}2$ atmospheres; and if the essure of a half-saturated solution of ammonia is it is found to be equal to 671 atmospheres at 0°; is obtained by the equation $0{\cdot}033\,P = 0{\cdot}0819 \times 273$ f the solution of ammonia contains one gram- *grams, of* NH_3). That the vessels wherein such kept are not shattered is to be accounted for by re, calculated in thousands of atmospheres, r the separate particles of the solutions. e could only gain the mastery, and walls of the vessels, if these walls were vessels were immersed in the solvent

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...ature whereat the experiment is
...of the mercury must not be read off
...utes, ...is necessary to let the
...t wet ...iently by repeatedly
...The ... of the barometric
...initial ...in the measurement
...as ...e quantity of vapour
...the ... the position of the
...tity of vapour. The
...arometer tube is not

rfectly free from air, or if the liquid under examination ntains impurities.

The value of the maximum vapour-pressure of a liquid a measure of the volatility of that liquid. The value for ter at 16° is 13·5 mm., while for ether it is 374 mm. at same temperature.

The depression of the mercury in the barometer tube is found be smaller when the liquid contains some other substance solved in it. The laws which express the lowerings of the our-pressures of solutions were elucidated experimentally Raoult (*Zeit. für physikal. Chemie*, **2**, p. 353 [1888]). work of that investigator was more fruitful than that is predecessors (Wüllner and Babo), because he began the more volatile solvents, and he paid especial attention ie solutions of those indifferent substances which did not uct the electric current, and which themselves exerted ur-pressures that were extremely small. Working by barometric method, Raoult arrived at the following *ments*:—

The relative depression of the vapour-pressure

$$\frac{p - p_1}{p}$$

the temperature, from 0° to 20°. In the he: vapour-pressure of the solvent alone, r-pressure of the solution.

of the vapour-pressure increases f dissolved substance, provided too large.

n of the vapour-pressure is ve depression to one gram- lved in 100 grams of the

where l is the quantity of the dissolved substance, in grams, and m is the molecular weight of the substance.

The molecular depression of the vapour-pressure has a constant value for solutions of different substances in the same solvent; it is dependent, like the osmotic pressure, only on the number of molecules of the dissolved substance that is present in the solution.

IV. If the number of molecules of the substance and the number of molecules of the solvent are expressed by n and N respectively (calculated by dividing the quantities by weight of substance and solvent by the respective molecular weights), then the following equation holds good for all solvents :—

$$\frac{p - p_1}{p} = \frac{n}{N + n}.$$

That is, the relative depression of the vapour-pressure, for any solvent, is equal to the ratio of the number of molecules of the dissolved substance to the total number of molecules of substance and solvent present in the solution.

Passing over the more accurate determinations of vapour-pressures which were made by Raoult, with materials that were purified very carefully, and by the use of the cathetometer for reading the levels of the mercury, and with all the necessary corrections, we may illustrate the law of proportionality—the relative depression of the vapour-pressure of a solution is proportional to the quantity of dissolved substance—by the following experiment.

Four barometer tubes of equal length, R_1, R_2, R_3, and R_4, figure 27, provided with millimetre scales, are filled with pure mercury, and are inverted in the mercury bath W and secured at equal distances apart. If all the air-bubbles have been removed, the levels of the mercury must be the same in the four tubes. Three very small flasks of the shape shown at F (such flasks as are used in Hofmann's vapour-density

nethod) are filled, one with pure ether, another with a solution
of 12·2 grams benzoic acid in 100 grams ether, and the third
vith a solution of 24·4 grams of the same
cid in 100 grams ether. The best way
f filling the little flasks is to attach them
o platinum wire, and to immerse them
1 the solutions contained in the flasks
herein these solutions have been pre-
ared, and as soon as the little flasks are
ll, to close them at once with their stop-
ers. The little flasks are then thoroughly
eaned externally by ether, and they are
lowed to rise, stoppered ends downwards,
d in the order stated above, to the top
the mercury in the tubes R_2, R_3, and
; the fourth tube, R_1, serves to measure
e pressure of the air. The levels of the
rcury become constant after a time, and
is then seen that if the levels are sup-
sed to be joined by a curve, the curve
l be a straight line, as is demanded by
laws of proportionality. Although the
nbers which are read off on the milli-
re scales are only approximately ac-
ıte, nevertheless they help towards an
erstanding of Raoult's law of propor-
ality. They may, therefore, find a
e in the following table, *Table VII.*,
de the data of other experiments and
calculations be longing thereto.

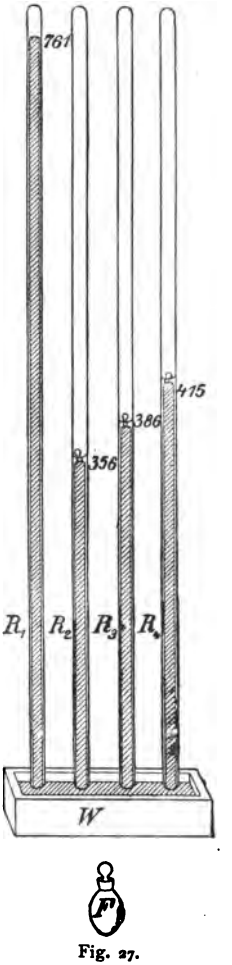

Fig. 27.

he numbers in columns 7 and 8 of *Table VII.* prove
oximately, the second and third laws of Raoult. T'
bers in column 9 agree fairly with those in column

numbers in column 10

the molecular depres-

the molecular weights of the

These numbers

gram-molecule of sub-

gram-molecules of solvent: they are

the value of

the dissolved substance can be

serve to control the

be the molecular

the solvent in grams,

substance in grams, then

grams the molecular weights

and naphthalene, calculated

in the other columns.

TABLE VII.

8	9	10	11	12
			Molecular weight.	
$\frac{p-p_1}{p}\cdot\frac{m}{l}$	$\frac{n}{N+n}$	$\frac{1}{74\,(78)}\cdot\frac{p-p_1}{p}\cdot\frac{m}{l}$	Calculated. $m=M\cdot\frac{l}{L}\cdot\frac{p_1}{p-p_1}$	Found by other methods.
0·740	0·0689	0·00999	113	122
·728	·1289	·00984	106	122
·762	·0689	·01030	124	138
·773	·1289	·01040	112	138
·762	·0723	·00977	121	128

Inasmuch as both osmotic pressure and relative depression vapour-pressure are constant for equimolecular solutions in e same solvent, it may be assumed that these o magnitudes are connected causally. As a atter of fact, van't Hoff has deduced the one w from the other by a thermodynamical lculation.

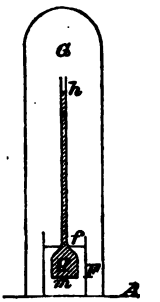

Fig. 28.

In a simpler way, Ostwald (*Lehrbuch der gemeinen Chemie*, i., p. 728 [1891]), following rhenius, has arrived at Raoult's law from the r of osmotic pressure; and his deduction may repeated here briefly. A small bell-shaped sel, *g* (figure 28), is closed beneath by a semipermeable mb and is fitted with an upright tube 1 centim. e vessel is poured a solution of *n* gram- ıe substance dissolved in *N* gram-molecules ıe vessel is immersed, as far as *f* in the pure in the receptacle *F*. The apparatus is , *A*, and it is covered with a bell-jar, *G* a vacuum is produced. The osmot ıe liquid to rise in the upright tut

say as far as h. The osmotic pressure is then given by the equation

$$P = \frac{nRT}{V},$$

where $R = 84{,}700$, P being measured in grams, and V in c.c. Expressing the molecular weight of the solvent by M, the weight of the solution is MN grams, as the weight of the dissolved substance may be neglected because of the small concentration of the solution; and, putting s as the specific gravity of the solution—and this must be very nearly equal to the specific gravity of the solvent—then V must be $= MN/s$ c.c. Consequently

$$P = \frac{nsRT}{MN}.$$

Moreover, if the distance fh, measured in centims., is represented by H, then $P = Hs$; and hence

$$H = \frac{nRT}{MN}.$$

But if the apparatus is in equilibrium, the vapour-pressure of the solution p_1, *at the point* h, *is equal to the vapour-pressure of the solvent* p, *decreased by the weight of a column of vapour of the length* fh *and* 1 *square centim. cross-section.* Hence, if d represents the weight of 1 c.c. of vapour, $p_1 = p - Hd$, or $p - p_1 = Hd$. Now v c.c. of vapour weigh M grams, when v is the molecular volume of the solvent in the form of vapour. Hence 1 c.c. vapour weighs M/v grams; or, as the gaseous equation $pv = RT$ is applicable.

$$d = \frac{Mp}{RT}.$$

Finally, by inserting the values for H and d in the equation $p - p_1 = Hd$, we get

$$p - p_1 = \frac{nRT}{MN} \cdot \frac{Mp}{RT} = \frac{n}{N}p;$$

or

$$\frac{p - p_1}{p} = \frac{n}{N}.$$

his is the equation found empirically by Raoult; provided hat n is very small in reference to N, that is, provided the olution is very dilute.

For limited concentrations H has an extremely high value, nd as d varies with H, the pressure π of the column of apour of the height H cannot be put down, offhand, as $= Hd$. Rather is $\delta\pi = d \cdot \delta H$; or, as $d = M\pi/RT$, then

$$\frac{RT}{M} \cdot \frac{\delta\pi}{\pi} = \delta H.$$

ntegrating this equation between 0 and H, we get

$$H = \frac{RT}{M} \log. \frac{\pi_0}{\pi_H},$$

nd in this $\pi_0 = p$ and $\pi_H = p_1$. But it has been found from he osmostic pressure that

$$H = \frac{nRT}{MN}.$$

ence

$$\frac{RT}{M} \log. \frac{p}{p_1} = \frac{nRT}{MN},$$

$$\log. \frac{p}{p_1} = \frac{n}{N}.$$

ut

$$\log. \frac{p}{p_1} = \log. \left(1 + \frac{p - p_1}{p_1}\right) = \frac{p - p_1}{p_1} - \frac{1}{2}\left(\frac{p - p_1}{p_1}\right)^2 + \ldots . \frac{p - p_1}{p_1}.$$

llows that

$$\frac{p - p_1}{p_1} = \frac{n}{N},$$

$$\frac{p - p_1}{p_1} = \frac{n}{N + n}.$$

*ula of Raoult is placed on a theoretical ula $PV = RT$, on which that way sts, is again justified.**

ag. [5], **42**, p. 289 (October, 1896), where at on the hypothesis of aggregation e dissolved substance.—[TR.]

[illegible] that, these

vo quantities will increase propor-
onately to the concentration, and
iat they will have the same value
r equimolecular solutions in the
me solvent.

As a matter of fact, experiments
ive led to this conclusion; and
was Raoult who succeeded in
olving this problem experi-
entally, especially by his investi-
ition of organic compounds, and
s statement of the results in
olecular quantities of these com-
ounds.

Inasmuch as the methods based
determinations of the boiling
oints and the freezing points of
lutions give more accurate esti-
ations of the molecular weights
the dissolved substances, and
more convenient to use, than
ethods dependent on measure-
nts of vapour-pressures, appara-
es of great delicacy and accuracy
ve been constructed from time
or the purpose of deter-
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Those described by
e used most com-
ir physik. Chemie, 2,
543). The appara-
in figure 29 is
determining the boiling points of aqueou

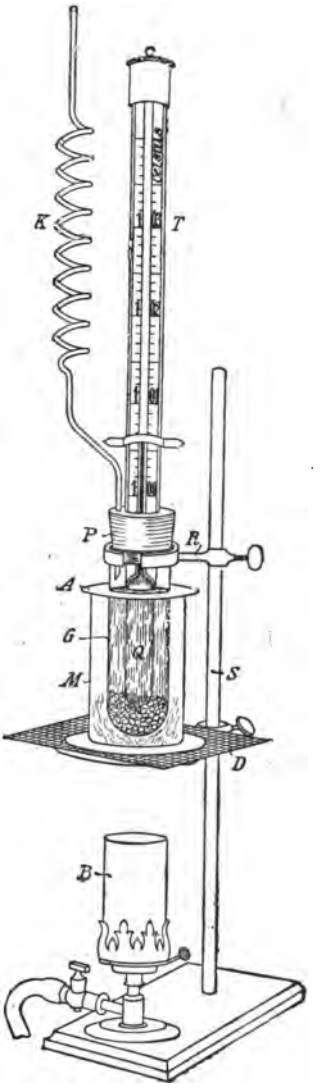


Fig. 29.

ling proceeds very regularly and quietly; the garnets ent bumping of the liquid, the air-mantle between *G* *M* forms a sufficient heat-guard, and only about one) of water flows per minute from the condenser. The ng point of a solution is determined by shaking a weighed ıtity of the substance to be examined, in the state of der, into the water, and proceeding as described.

able VIII. presents the results obtained with an aqueous ion of cane sugar; *l* shows the grams of sugar in 100 ıs of water, *b* the height of the barometer in mm., t_0 the ng point of water, *t* the boiling point of the solution, ıe molecular weight of cane sugar (342), and *S* the cular increase of boiling point referred to 100 grams of olvent.

TABLE VIII.

2	3	4	5	6	7	8
b	t_0	t	$t-t_0$	$\frac{t-t_0}{l}$	$S=\frac{t-t_0}{l}\cdot m$	$m=S\frac{l}{t-t_0}$
mm.						
746	99·85°	100·35°	0·50°	0·01462	5·00°	342·0
746	99·85°	100·59°	0·74°	0·01442	4·93°	341·7
755	99·90°	100·95°	1·05°	0·01535	5·24°	341·3
755	99·90°	101·22°	1·32°	0·01544	5·28°	342·0

: numbers in column 6 show that the increase of the g point is constant for each 1 per cent. of sugar—led the solutions are not too concentrated; that is to

g point increases in proportion to the concentration.

f *S* in column 7 indicate that the *boiling olecular solutions are increased to the same*

constant *S* has been found for a determinate ıse of a substance whose molecular weig

e molecular weight *m* of another substa

dissolved in the same solvent can be found by the equation $l : m = t - t_0 : S$. Column 8 contains the values of m, for sugar, calculated from the values found for l and $t - t_0$; the values of m agree very closely, and are nearly equal to the true value 342. If L grams of solvent are used, in place of 100 grams, then

$$m = 100\, S \frac{l}{L(t - t_0)}.$$

Troublesome though it is to determine the boiling points of aqueous solutions during a lecture, these boiling points have a very especial interest in connection with electrolysis (see Chapter V.). The experiments with cane sugar which have been described may be turned to further account, as it is possible to invert the cane sugar in accordance with the equation

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

by adding a c.c. of hydrochloric acid containing potassium chloride to the boiling solution, and so to double the number of molecules in solution in less than a minute, and hence to bring about double the increase of the boiling point.

In making determinations of molecular weights by the boiling-point method, care must be taken to select solvents which are without chemical action on the dissolved substance.

The boiling-points, and the values of S, of various solvents are as follows:—

	Water.	Alcohol.	Ether.	Acetic acid.	Ethyl acetate.	Chloroform.
$t_0 =$	100°	78·3°	34·97°	118·1°	72·8°	61·2°
$S =$	5·2°	11·5°	21·1°	25·3°	26·1°	36·6°.

When one of these liquids other than water is used, thermometers with smaller bulbs may be employed, because of the higher values for S for these liquids. Experiments may

therefore be conducted more rapidly with these liquids. The apparatus represented in figure 30, which is of more simple construction than that shown in figure 29, may be employed for the purposes of demonstration. The bulb of the boiling vessel G is of 200 c.c. capacity; its neck is 30 centims. long and 3 centims. wide. The vessel is placed in a basin made of asbestos lined with asbestos-wool, S, and it must be surrounded by a mantle, M, made of thick woollen cloth (as shown in the figure) to protect it from the effects of possible draughts of air. The cork k carries the thermometer T, and the two long serpentine condensers K_1 and K_2 between the bends of which wetted filter paper should be placed. The bulb of the thermometer (50 × 8 mm.) reaches so far into the boiling-vessel that the end of it touches the surface of the 100 grams of solvent placed in that vessel. The thread of mercury is 2 mm. broad; it may therefore be seen from a considerable distance. The scale begins at 30°; and from 30° to 110° it is 30 centims. in length, so that each degree is represented by nearly 4 mm., and tenths of a degree can be read off. Delay in boiling is avoided in the way already

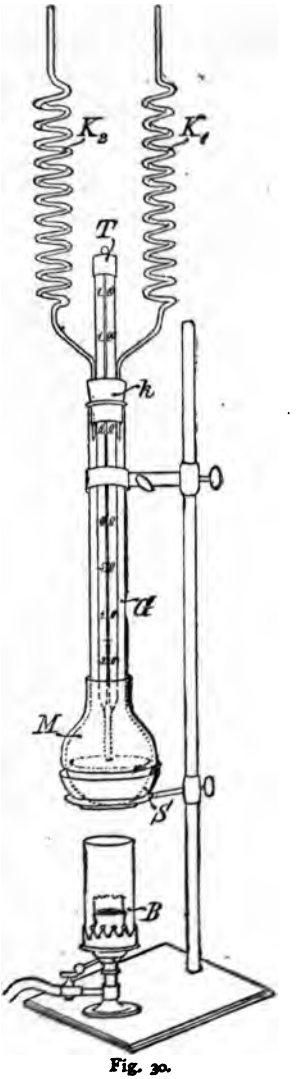


Fig. 30.

described (p. 100). An Argand burner with a luminous flame, provided with a tall chimney and a regulating stopcock, is recommended for heating. The boiling point of the solvent is determined first of all, and the substance to be dissolved is then added through the neck of the boiling-vessel.

Table IX. contains the results of determinations of the boiling points of solutions of naphthalene (mol. wt. 128) in ethylacetate.

TABLE IX.

l	t_0	t	$t-t_0$	$\frac{t-t_0}{l}$	$S=\frac{t-t_0}{l}\times m$	$m=26{\cdot}1\times\frac{l}{t-t_0}$
grams.						
3·2	72·8°	73·5°	0·7°	0·2188	28·00°	119·3
6·4	72·8°	74·1°	1·3°	0·2031	25·99°	128·5
9·6	72·8°	74·7°	1·9°	0·1979	25·33°	125·3

Decidedly fewer precautions are required in determinations of the freezing points of solutions than in determinations of their boiling points. Several years ago Ciamician (*Zeit. für physik. und chem. Unterricht*, **3**, p. 39) described a process by which lowerings of freezing points might be illustrated qualitatively by the use of an air-thermometer, But as the air-thermometer cannot be adjusted readily, the demonstration-thermometer T (fig. 31) is to be recommended.* This instrument is useful for many other purposes, such as determinations of the heats of solution of salts and the specific heats of metals. The bulb is 14 centims. long, and only 1·5 centim. wide; it is filled with amylic alcohol coloured blue. The scale is 60 centims. long; it extends

* Made by glass-blower Stühl, Berlin N., Philippstrasse 22; price 12 marks.

over 75°, from 30° under to 45° above zero. As each degree is 8 mm. long, tenths of a degree can be read off with ease. This thermometer is placed in the vessel R (wherein the freezing is effected), which has the form of a test-tube. The level of the solution under examination must be coincident with that of the bulb of the thermometer, and must be distant 3 centims. from the rim of the vessel R. The tube R is fastened in the opening of the flask F by means of a disc of cork. The flask F is filled with a concentrated solution of calcium chloride in glycerin or alcohol, and is placed in a cooling bath, K, of 5 to 6 litres capacity. To obtain approximately accurate results with this apparatus, the sensitiveness of which can only be somewhat small, it is necessary to work with solutions such that the freezing points to be observed are not very low, and the stirrer r (which is made of nickel) must be kept constantly in motion until the solvent separates in the solid form. The process of cooling must in no case be conducted very quickly; and it is therefore necessary that the temperature of the solution of calcium chloride should not be more than 2° or 3° lower than that of the freezing point of the solvent. This can be brought about easily, inasmuch as the proper temperature can be produced in the cooling bath K by using ice-water, or a mixture of ice with more or less common salt, according to the circumstances of the experiment.

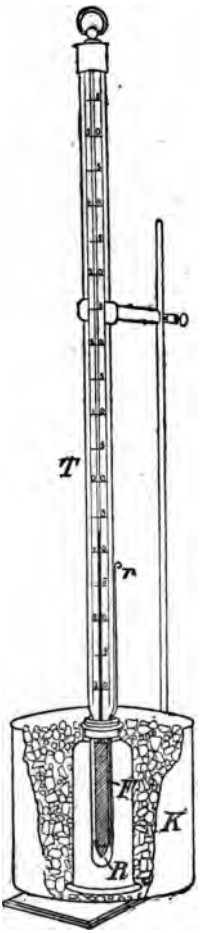


Fig. 31.

			10
			3420
			1195
			1280
			930
			1220

the boiling and

ed by these results.

with concentration

the freezing point has the

an value of 18·5° for water, and 49° for benzene, when one .m-molecule of substance is dissolved in the same quantity ıO grams) of either of these solvents (columns 7 and 8). at the depression of the freezing point is dependent only the number of molecules of substance present in a constant antity of the solvent may also be illustrated by inverting : 34·2 per cent. solution of cane sugar, and then bringing : solution again into the freezing apparatus, when θ will found to be $= -3{\cdot}3°$. The numbers in columns 9 and 10 licate the importance of determinations of the freezing ints of solutions as means for finding molecular weights. ıe molecular weights are calculated by the equations:—

$$l : m = \theta_0 - \theta : G$$

$$l : m = (\theta_0 - \theta)\ \mathrm{L}/100 : G,$$

ıere L expresses the quantity of solvent used in the special periment.

The values of G for various solvents, determined by Raoult :—

	Water.	Acetic acid.	Formic acid.	Benzene.	Nitro-benzene.
$\theta_0 =$	0°	20°	8·5°	4·9°	5·3°
$G =$	18·5°	38·6°	27·7°	50·0°	70·7°.

The results obtained by the boiling-point method and by e freezing-point method show differences from the numbers lculated from the theory; these differences cannot be ferred altogether to the errors inherent in the methods. ıe numbers obtained by the use of Beckmann's apparatus ten deviate very markedly from the theoretical values. The lues of $(\theta_0 - \theta)/l$ decrease, as a rule, proportionally to con-ntrations, for solutions in benzene; this is explained by t sumption, which is well founded, that some of the molecu

CHAPTER IV.

SUMMARY.

THE investigations made regarding dilute solutions have led, so far, to four laws of similar import. These laws are as follows: *Equimolecular solutions of any substances, prepared by using equal weights of the same solvent, exhibit equal osmotic pressures, equal relative depressions of vapour-pressure, equal raisings of boiling point, and equal lowerings of freezing point.* The experimental data allow the inversion of these laws. The magnitudes P, $(p - p_1)/p$, $t - t_0$, and $\theta_0 - \theta$ must, therefore, be proportional to one another for relatively equal concentrations, which are, however, generally small concentrations, and the factor of proportionality can be dependent only on the constants of the solvent. Van't Hoff (see Nernst's *Theoretical Chemistry* [English Ed.], pp. 126, 128) elucidated the relations between osmotic pressure and the three other magnitudes; and he established the following equations, in which M is the molecular weight, and s is the specific gravity, of the solvent, T_0 and T_0' are its absolute boiling point and freezing point respectively, w and w' are the latent heat of evaporation and the latent heat of fusion of the solvent per gram, and K, K', and K'' are collective constants depending on the solvents used.

$$\text{I. } P = \frac{p - p_1}{p_1} \times \frac{819 s \cdot T}{M} = \frac{p - p_1}{p_1} \text{TK atmos.}$$

$$\text{II. } P = (t - t_0) \times \frac{41{\cdot}37 \cdot s \cdot w}{T_0} = (t - t_0)\ \text{K}' \text{ atmos.}$$

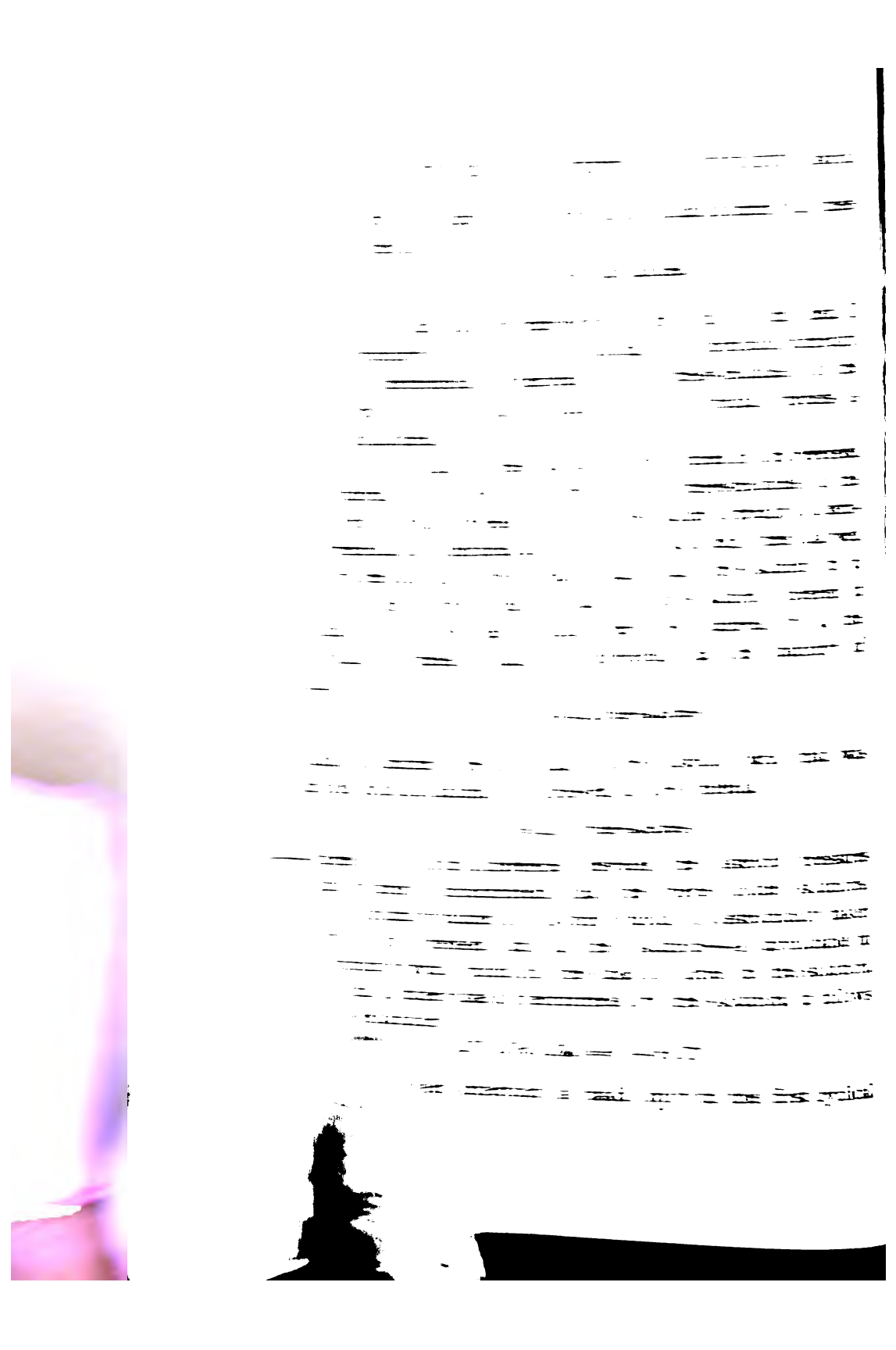
$$\text{III. } P = (\theta_0 - \theta) \times \frac{41{\cdot}37 \cdot s \cdot w'}{T_0'} = (\theta_0 = \theta)\ \text{K}'' \text{ atmos.}$$

determinations can be accomplished much more accurately than measurements of osmotic pressure, satisfy the equation $PV = RT$, which corresponds with the gaseous equation; *hence the theory of van't Hoff is confirmed afresh by the methods of boiling and freezing points.* Moreover, testimony to the justness of this theory is borne by the fact that the same molecular weights are found for substances in solution from determinations of the boiling and freezing points of the solutions as those which are arrived at by measurements of vapour densities.

Another very convincing argument in favour of the theory of solutions has been given by van't Hoff, by his demonstration that the values arrived at for the molecular depressions of freezing points by purely thermodynamical considerations based on the gaseous equation are the same as those that are determined empirically. Let the following reversible process be imagined. A solution of n gram-molecules of a substance in a *very large number*, N, of gram-molecules of a solvent is at the temperature θ_0, and is cooled to θ. In the process of cooling so much heat is withdrawn that N/n gram-molecules of the solvent, that is, the quantity in which one gram-molecule of the substance is dissolved in the original solution, freeze out. Hence $N/n.\ M\omega$ gram-calories will be set free, at θ, when ω represents the latent heat of fusion at θ. Let it be supposed that the quantity of the solvent which is frozen is removed from the solution, is heated to θ_0, and is melted at θ_0. In doing this $N/n.\ M\omega'$ gram-calories will be taken up, when ω' is the latent heat of fusion of the solvent at θ_0. Now, as latent heats of fusion are smaller at lower temperatures, it is true that

$$\frac{N}{n} M\omega < \frac{N}{n} M\omega'.$$

If the remaining solution is brought, meanwhile, to θ_0, the



rocess ; for, in accordance with the second law of the ynamical theory of heat, when heat does work in a eversible cyclical process, the portion of this which is hanged into work is related to the total quantity of heat dded to the system as the fall of temperature is related o the absolute temperature whereat the heat is taken up y the system.

It follows from the foregoing equation that

$$\theta_0 - \theta = \frac{2nT_0'^2}{MN\omega'}.$$

But if one gram-molecule of substance is dissolved in 100 gram-molecules of the solvent, then

$$\theta_0 - \theta = \frac{0{\cdot}02T_0'^2}{\omega'},$$

where T_0' is the absolute freezing point of the solvent, and ω' (which differs but slightly from ω) is the latent heat of usion of the solvent, calculated for one gram. Now the value found for this quantity $\theta_0 - \theta$ is identical with the empirically determined quantity G. For instance, taking the solvent water, and putting T_0' as 273, and ω' as 79, the value for $\theta_0 - \theta$ is 18·8, while experiment gives $G = 18{\cdot}5$.

A corresponding equation has been deduced by van't Hoff for the molecular raising of boiling point referred to 100 grams of solvent ; this formula is

$$t - t_0 = \frac{0{\cdot}02T_0^2}{w},$$

T_0 is the absolute boiling point, and w is the latent evaporation, of the solvent. This equation satisfies ts of experimental measurements.

, it is to be remarked that the quantities ω an lculated from the two equations, using the empi

CHAPTER V.

AQUEOUS SOLUTIONS OF ELECTROLYTES.

ATTENTION has already been drawn to the fact that the investigations which led Raoult to the laws that have been stated in the last chapter, which laws were placed on a theoretical foundation by van't Hoff, were carried out with solutions of indifferent organic compounds in water or in organic solvents. Many substances, namely, the salts, acids, and bases, and especially inorganic compounds of these classes, exhibit, when in aqueous solutions, deviations from these laws, and these deviations at first militated against the general recognition of van't Hoff's theory. The values of the quantities P, $(p-p_1)/p$, $t-t_0$, and $\theta_0-\theta$, are higher in these cases than the theory requires. The first and second quantities cannot, however, be measured with sufficient accuracy to enable any kind of regularity in their deviations from the laws to be recognised with certainty. For, on the one hand, membranes of copper ferrocyanide are no longer completely semipermeable at the high pressures that these compounds exert, and, on the other hand, the differences in the vapour pressures of aqueous solutions of the compounds are too small. But further light has been thrown on the matter by investigations into the boiling and freezing points [of solutions of these classes of compounds]. The results of some investigations, made as described in Chapter III.,

are gathered together in *Tables XIII.* and *XIV.*, the same symbols being used as before.

TABLE XIII.

1	2	3	4	5	6	7	8	9	10
Substance in 100 grams water.	l	$t-t_0$	$\frac{t-t_0}{l}$	m	$S=\frac{m.t-t_0}{l}$	$i=\frac{S}{5{\cdot}2}$	$i''=1+(s-1)\frac{\lambda}{\lambda\infty}$	$\alpha=\frac{i-1}{s-1}$	$\alpha''=\frac{\lambda}{\lambda\infty}$
Sodium chloride	5·85	0·94	0·160	58·5	9·36	1·80	1·82	0·80	0·82
" "	8·80	1·40	0·159		9·30	1·78		0·78	

TABLE XIV.

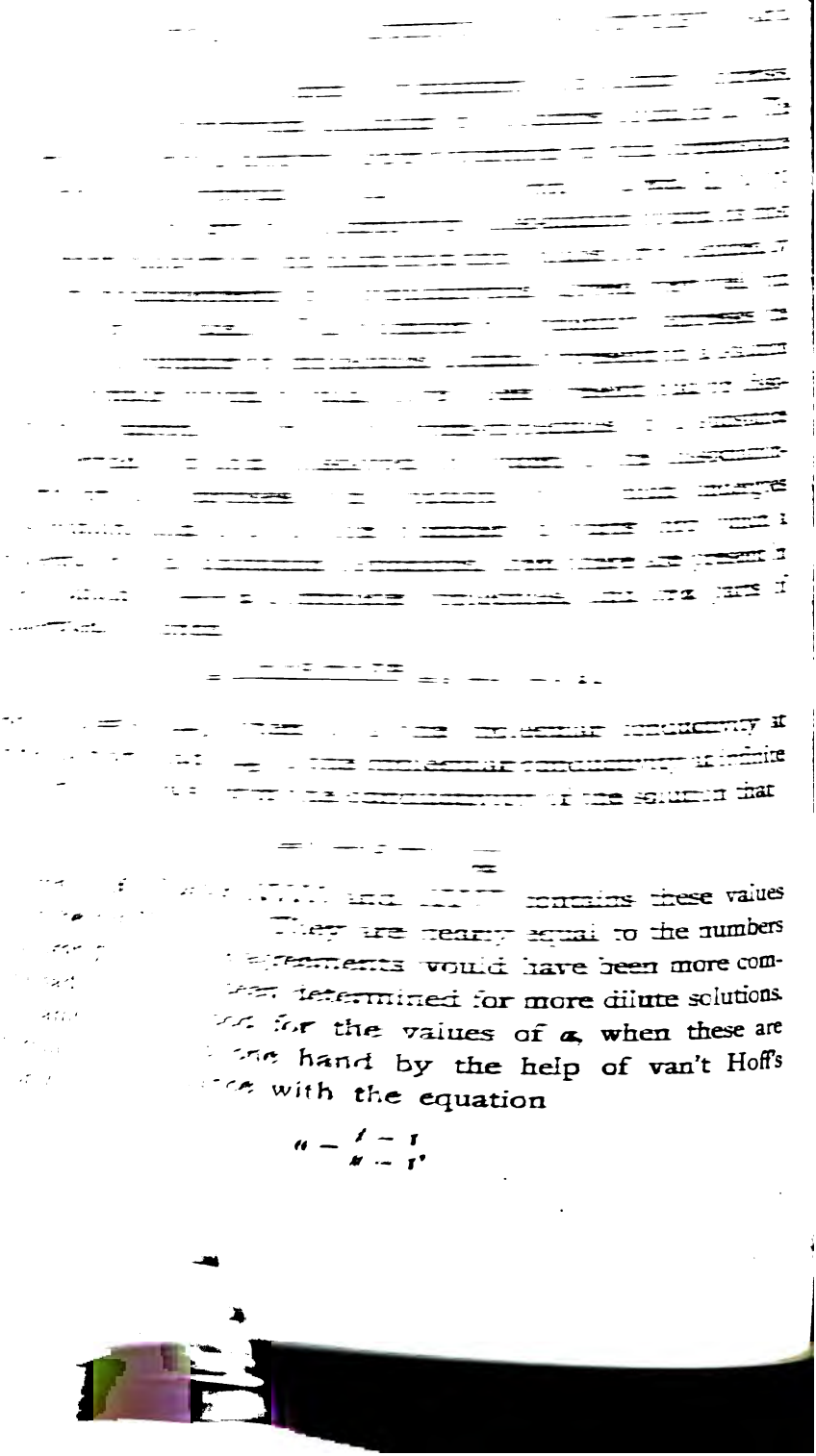
1	2	3	4	5	6	7	8	9	10
Substance in 100 grams water.	l	$\theta_0-\theta$	$\frac{\theta_0-\theta}{l}$	m	$G=\frac{m.\theta_0-\theta}{l}$	$i'=\frac{G}{18{\cdot}5}$	$i''=1+(s-1)\frac{\lambda}{\lambda\infty}$	$\alpha'=\frac{i'-1}{s-1}$	$\alpha''=\frac{\lambda}{\lambda\infty}$
Sodium chloride	5·83	3·5	0·598	58·5	34·98	1·89	1·82	0·89	0·82
" "	8·80	5·2	0·591		34·51	1·87		0·87	
Potassium chloride	6·00	2·7	0·442	74·58	32·97	1·78	1·86	0·78	0·86
" "	10·00	4·4	0·440		32·81	1·77		0·77	
Calcium chloride $CaCl_2 . 6\,H_2O$	21·90	5·2	0·237	219·98	51·90	2·69	2·50	0·84	0·75

The numbers in column 3 show that the values both of $t-t_0$ and $\theta-\theta_0$ increase for each substance as concentration increases. Moreover, the molecular depressions of the freezing point G (column 6) agree for the solutions of sodium chloride. The values for S and G, however, are greater, on the whole, than the values for S and G in *Tables VIII.* and *X.* (pp. 111, 116). What multiples of the normal values, 5·2 and 18·5, these numbers are, is discovered by dividing the numbers by 5·2 and 18·5 respectively. The quotients thus obtained (column 7) are designated by the letter i by van't Hoff. Now it has been found that the value of i for any substance

ıcreases with increasing dilution, and that the values of i re finally expressible by whole numbers 2, 3, 4 . . .; and, ıoreover, it has been shown that these values are equal ır substances of similar composition; for instance, i is equal ı 2 for the acids H′A′, the bases B′ (OH′), and the salts 'B′; and i is equal to 3 for the acids H'_2A'', the bases $''(OH')_2$, and the salts A'_2B'' and $A''B'_2$. The same results e obtained whether the values of i are found by the method osmotic pressure or by that of vapour-pressure, boiling ıint, or freezing point. Inasmuch as the quantities $(p-p_1)/p$, $-t_0$, and $\theta_0-\theta$ are proportional to the values of P, van't off was led to write the general equation in the form

$$PV = iRT.$$

The solutions of all these substances behave as if a greater mber of molecules were present than corresponds with the centrations. The analogy between solutions and gases ggested an explanation of these phenomena by supposing : occurrence of a dissociation of the molecules of the solved substances. The anomalous behaviour of certain es, such as nitrogen peroxide and phosphorus penta- oride, which showed a greater pressure than was demanded Avogadro's law, had been explained by the hypothesis of sociation. *Nevertheless, the resolution to employ this expedient he case of solutions would hardly have been come to had not substances in question been found to be electrolytes, and had the theory of electrolysis supported the demand for this ex- tation.* As a matter of fact, abnormalities in the phenomena he boiling point and freezing point appear only when the tions conduct the electric current. A solution of sodium ate in ether, or of potassium chloride in alcohol, behaves as normally as an aqueous solution of sugar or urea; tha' ıe factor $i = 1$. But as soon as these salts are dissolve



contains these values
are nearly equal to the numbers
measurements would have been more com-
determined for more dilute solutions.
for the values of α, when these are
hand by the help of van't Hoff's
with the equation

$$\alpha = \frac{i - 1}{n - 1}$$

and, on the other hand, by the equation $\alpha = \lambda/\lambda_\infty$. (See columns 9 and 10 of *Tables XIII.* and *XIV.*) With regard to the actual signification of the quantities α, it is to be remembered that 100 times the value of α represents the number of molecules of the substance dissociated out of every 100 molecules. The number ·89 for sodium chloride, for instance, tells that in the solution under consideration 89 per cent. of the molecules are broken up. *The parts of the molecules of a binary substance must certainly be identical with the ions, and because of the agreement between the values found for* i *by the two methods already mentioned, the parts of the molecules of all other electrolytes must also be identical with the ions.* The fact, made apparent by the results in *Tables XIII.* and *XIV.*, that the degree of dissociation decreases with concentration, a fact which must follow from the data concerning conductivities, also points in the same direction. Arrhenius has thus explained the peculiar behaviour of aqueous solutions of electrolytes in terms of the law of van't Hoff, although that behaviour seemed at first sight to be opposed to the law; and by doing this he has not only demonstrated the applicability of Avogadro's law to electrolytic solutions, but he has also established the correctness of his own theory of dissociation.

PART III.

THE IONIC THEORY OF THE CURRENT IN GALVANIC CELLS.

SEVERAL propositions have been laid down in the first and second parts of this book, the justness of which has been established almost entirely by experimental evidence. Nernst based his theory of the production of the electric current in galvanic cells on these propositions. That theory, and the deductions made from it, will be considered in this part of the book.

CHAPTER I.

LIQUID CELLS.

HE fact has been known for long that electrical differences e perceived when conductors of the second class are brought to contact. It was not, however, to be supposed that the ere contact was the cause of these phenomena.

Nernst explains the occurrence of a difference of potential tween solutions, of different concentrations, of the same ctrolyte, by the different velocities of the ions set in tion by osmotic pressure, whereby the kations become sent in excess in one solution and the anions in the other ution. Inasmuch as the ions bear electric charges with m, an accumulation of positive electricity is brought about solution and of negative electricity in the other; and different electrodes are placed in the solutions and d by a wire, a current must be produced in the use of the equalisation of the two electricities. Cells id a- -all d *liquid cells.*

n, submitted by H. von Helmholtz, to of Sciences in 1889, Nernst calculated ntial of liquid cells on the supposition *Sitzungsber. der Kgl. preuss. Akad. d.* necessary to make a brief repetition ssions, as they form the basis of th urrent. To simplify matters let

[redacted]

of work expressed by $\int_{p_1}^{p_2} V\,dp$ must be-

when the volume of a solution, V, which
am-atom of kation passes from the osmotic
the lower pressure p_2. Therefore, $u/(u+v)$
f kation accomplish the work

$$\frac{u}{u+v}\int_{p_1}^{p_2} V\,dp,$$

$= RT$, that amount of work is equal to

$$\frac{u}{u+v}RT\int_{p_1}^{p_2}\frac{dp}{p},$$

$$\frac{u}{u+v}RT\log.\frac{p_1}{p_2}.$$

work to be done in raising $v/u+v$ gram-atoms of
m the pressure p_2 to the pressure p_1 is

$$\frac{v}{u+v}RT\log.\frac{p_1}{p_2}.$$

al work available from the osmotic energy is therefore

$$\frac{u-v}{u+v}RT\log.\frac{p_1}{p_2}.$$

f this work is changed entirely into the electrical energy
of work during the passage out of the vessel. It raises the a
on 800 square centims. to a height of 10 centims.; that is to
orms an amount of work equal to 1033 . 800 . 10 gram-centi-
. 8 kilo-decims. = 8 litre-atmospheres. If the same qu-
scapes again, the remaining gas is at the pressure of 3 at
he total work is equal to 8 (5 − 3) = 16 litre-atmospheres
1 gram-molecule of a gas, occupying a spac
of p_1 atmospheres, falls to the pressure of
mount of work expressed by

$$\int_{p_1}^{p_2} V\,dp$$ litre-atmosphere

[redacted]

[redacted]

[redacted]

A perfectly general formula, which includes the case of two different electrolytes in contact with one another, has been given by Planck; but that equation need not be considered here.

The fact is, however, to be emphasised that Nernst has confirmed his theory of liquid cells, in a more extended way, by experiments. Consequently, in such a cell osmotic energy performs electrical work. Chemical energy does not come into play in this case. One might expect that the current of this cell would continue until the osmotic pressures of the two solutions were equalised. But the ions must be constantly giving up their charges to the electrodes. And, as an electrostatic equilibrium very soon results between the kations and the anions, which equilibrium cannot be upset by the electromotive force of the cell, which is generally very small, the current of the cell must very soon cease.

The experimental demonstration of liquid cells may be omitted, because of the small values of the differences of potential of these cells.

[redacted]

[redacted] the

current is conducted from without, so in a galvanic cell, the electrodes are called the kathode and the anode respectively, according as the kations or the anions travel to them, and *in every case the (positive) current makes its way from the kathode through the connecting wire to the anode.* By keeping this firmly in the memory, errors in the use of the conceptions of positive and negative poles are easily avoided. The positive pole of a galvanic cell is that to which the kations proceed, and the positive pole of the source of a current is to be reached to that electrode of a decomposition-cell from which the kations must travel with the current towards the other electrode. *The positive current always goes in the same direction as the kations, both in the source of the current and in the decomposition-cell.* Inasmuch as the kations are discharged at the kathode, the name discharging-electrode is sometimes given to the kathode, and the anode is called the solution-electrode when the anions dissolve this electrode.

Three separate differences of potential come under consideration in a concentration-cell; one is that between the two solutions, and the two others appear at the surfaces between the metal and the electrolyte. Nernst has calculated the difference of potential between the metal and the electrolyte, and has given an explanation of the origin of this difference. For this purpose he introduced the conception of *electrolytic solution-pressure* (see contribution already cited [1] and also *Zeit. für physik. Chemie*, 4, p. 129 [1889]). [illegible] evaporates from its surface until the pressure of the vapor produced is equal to the evaporation-pressure [illegible] inasmuch as evaporation and solution are [illegible]es, a salt must dissolve in water until the [illegible] of the solution is in equilibrium with the [illegible]ssure of the salt in question. Simila[illegible] each metal, according to Nernst a f[illegible]

conditioned only by the chemical nature of the metal, which tends to dissolve metallic atoms in the form of ions. This force, which is called the solution-pressure, comes into play when the metal is immersed in an electrolyte, and it is the greater the fewer the kations already present in the solution. Putting P as the solution-pressure of a metal, and p as the osmotic pressure of the kations in the solution, three cases are to be distinguished. In the first case P may be greater than p; the metal then behaves like a quantity of salt added to an unsaturated solution of that salt. Kations tend to go into solution; and, as positive electric charges are transported by the kations while an equal quantity of negative electricity remains in the metal, the electrolyte acquires a positive, and the metal a negative, potential. However much the value of P may exceed that of p, the number of kations produced by the mere immersion of the metal in the electrolyte can be but small. For the kations collect on the bounding surface between the metal and the electrolyte, by reason of the electrostatic attraction of the kations by the negatively charged metal, and so work against the solution-pressure. Nevertheless, as soon as the free electricities are conducted away through a connecting wire, the solution-pressure manifests itself again, and continues to operate in the way already set forth until p attains the same value as P.

In the second case, when $P = p$, no difference of potential comes into play.

When, finally $P < p$, the metal corresponds with a quantity of solid salt brought into a supersaturated solution of that salt. Some of the kations now give up their charges to the metal; the metal therefore becomes charged positively, and the electrolyte acquires a negative potential. The process continues but a short time, until the positively charged metal, in its turn, repels the kations that come near it.

The theory of Nernst regards the conception of the solution-pressure of a metal as analogous with that of osmotic pressure. This hypothesis would lead us to expect that the difference of potential, $\mathfrak{p}$, between a metal and the solution of one of its salts, at a definite temperature, should be dependent only on the ratio P/p.

The following formula is arrived at by a method similar to that set forth for liquid cells :—

$$\mathfrak{p} = \frac{\cdot 0002}{n} T \log. \frac{P}{p} \text{volt} \quad \ldots\ldots\ldots\ldots\ldots \text{II.},$$

hen n is the valency of the kation, and $\mathfrak{p}$ is supposed to be the direction from the metal to the solution.

In the case of a concentration-cell of the form

$$M|MS \text{ conc.} \,/\, MS \text{ dil.} \,/\, M,$$

ere S represents the anion, the total difference of potential, s calculated from the algebraic sum of the three single rences of potential, by means of the equation

$$\pi = \frac{\cdot 0002}{n} T \left[\log. \frac{P}{p_1} + \frac{u-v}{u+v} \log. \frac{p_1}{p_2} - \log. \frac{P}{p_2} \right] \text{volt}$$
$$= \frac{\cdot 0002}{n} \cdot \frac{2v}{u+v} \cdot T \log. \frac{p_1}{p_2} \text{volt} \quad \ldots\ldots\ldots \text{III.}$$

condition which is assumed in calculating π, namely, he electrolyte is completely dissociated, is not fulfilled, rmula runs thus :—

$$\cdot 002 \cdot \frac{i}{n} \cdot \frac{v}{u+v} T \log. \frac{p_1}{p_2} \text{volt} \quad \ldots\ldots \text{IV.},$$

Hoff's factor. If $u = v$ the equation takes

$$\frac{i}{n} T \log. \frac{p_1}{p_2} \text{volt} \quad \ldots\ldots\ldots\ldots \text{V.}$$

aller, and if $u < v$ then π is greater, t

weight of silver are dissolved from A. The process continues, with the gradual falling off of the electromotive force of the cell, until the concentrations of the solutions are equalised, and, consequently, the osmotic energy is completely exhausted.

The experimental arrangement represented in figure 32 serves to detect the concentration-current by the help of a good galvanometer. The glass tube R, which is 15 centims. long and 2·5 centims. diameter, is filled to a b with a normal

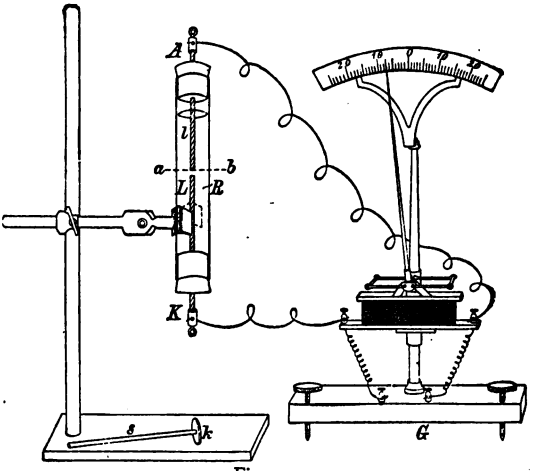


Fig. 32.

solution of silver nitrate; a layer of water is poured on to the surface of this solution by the use of the glass rod s, on the end of which is fastened the cork disc k; the electrode A is immersed in the liquid, and the lecture-galvanometer G, the magnet of which is furnished with a vertical wooden needle, is placed in the circuit.* The needle

* This galvanometer can be obtained from Keiser and Schmidt, Berlin (Johannesstrasse 20), for 55 marks. The instrument that was used in most of the following experiments, wherein weak currents had to be detected, has a resistance of 9·6 ohms, and is so delicate that a current of ·000226 ampère causes a deviation of one degree on the scale.

resents both electrodes, and at the same time the con-
ting wire also. The loss of metal at the upper end of
rod is well shown in the figure.

he effect of the difference of concentration of the solu-
is is made very evident by the following cell:—In the
formed tube (figure 34) are placed the mercury electrodes
and K, which are connected with the conducting wires
platinum wires fused into the glass. The obliquely
ected tube which joins the limbs S_1 and S_2 contains a
pper of glass wool. If a cold saturated
ution of commercial crystallised mercurous
rate is poured into the apparatus to the level
n, the needle of the galvanometer remains
rest, because $p_1 = p_2$. But if a concentrated
lution of potassium chloride is now poured,
tle by little, into the limb S_1, and immediately
terwards the corresponding volume of mer-
rous nitrate is poured into S_2 for the purpose
restoring equilibrium, the needle shows a
eviation, which is greater the greater the
uantity of potassium chloride that is added.
Mercurous chloride is precipitated in the
mb S_1, in accordance with the equation
$HgNO_3 + KCl = HgCl + KNO_3$, and the concentration of the
ercury ions is hereby decreased. In this way a concen-
cell is produced, wherein it can be easily shown
accordance with *Formula IV.*, π increases as p_2
. In a few minutes the needle returns to the zero
he anode becomes covered with the mercurous
ich rapidly sinks to the bottom of the vessel.
recipitate is stirred by a glass rod, and is thus
suspension, the needle at once moves to i
n.

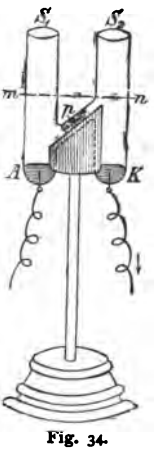
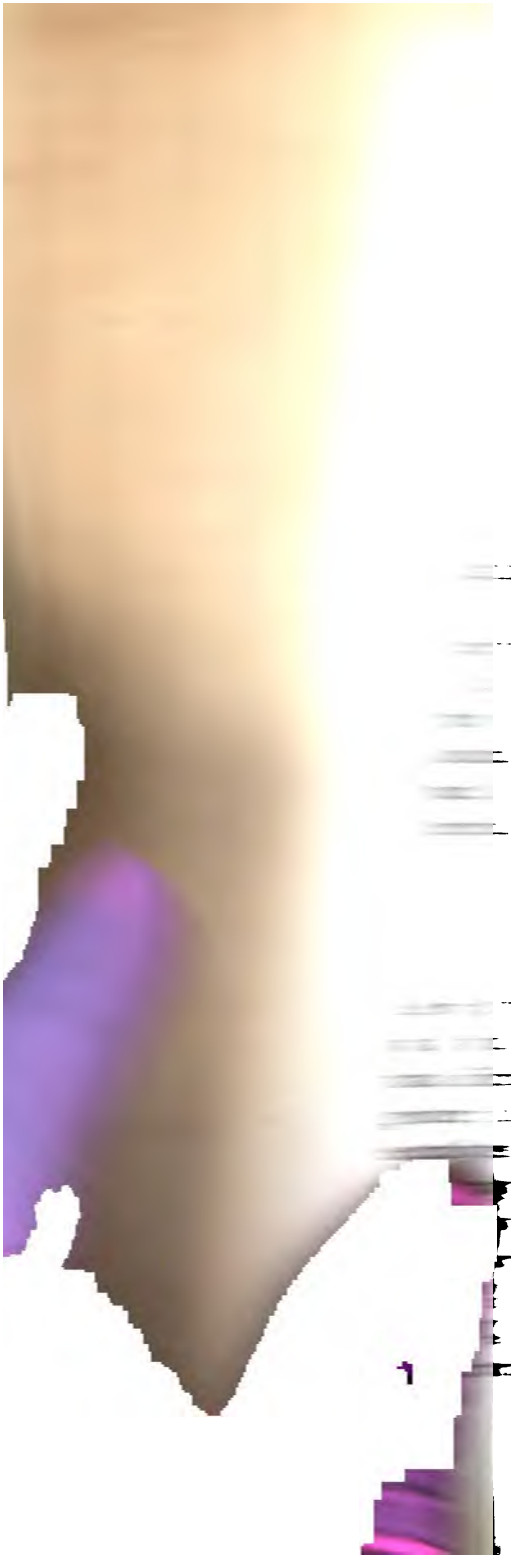


Fig. 34.



metals,

and n the valency of the metals taken as of equal valency, it follows, in accordance with *Formula II.* (p. 139), that

$$\pi = \frac{\cdot 0002}{n} T\left(\log. \frac{P_1}{p_1} - \log. \frac{P_2}{p_2}\right) \text{ volt} \quad \ldots\ldots \text{VI.}$$

$$= \frac{\cdot 0002}{n} T\left(\log. \frac{P_1}{P_2} - \log. \frac{p_1}{p_2}\right) \text{ volt} \quad \ldots\ldots \text{VII.}$$

And if the valencies of the metals are different, then

$$\pi = \cdot 0002\, T\left(\frac{1}{n_1} \log. \frac{P_1}{p_1} - \frac{1}{n_2} \log. \frac{P_2}{p_2}\right).$$

The direction of the current within the cell is taken as from M_1 towards M_2.

There are various methods for measuring the electromotive force of the source of a current. When the circuit is open, the measurement is made by a quadrant electrometer, by observing the deviation of the needle, proportional to the electromotive forces, which is brought about on the one hand by the cell to be tested, and on the other hand by a normal element (for instance, a Clark element $Zn/ZnSO_4/Hg_2SO_4/Hg$, for which $\pi = 1{\cdot}438$ volt at 15°). The E.M.F. of a closed cell is read off directly on a sensitive galvanometer, furnished with a high resistance (about 10^5 ohms), and graduated to volts by means of a normal element. Poggendorff's compensation-method is generally used for more accurate electrochemical work. One of the more simple forms in which this method is used is represented diagrammatically in figure 35: $a\ b$ is a measuring wire, 1 metre long, of about 50 ohms resistance; A is a constant source of current, the E.M.F. of which, E, is known and is greater than that to be measured; $b\ c$ is a variable resistance which must be sufficiently large to ensure that E does not vary when A is connected with a and c. Under these conditions the slope of the potent[ial] along the line $a\ b$ is perfectly definite; when, for instan[ce]

$E=2$ volts, it amounts to 0·2 volt, and hence to 0·0002 volt per millimetre of the measuring wire. The source of current B and the galvanometer G are connected with the measuring wire so that the currents meet at a. If the sliding contact d is moved until the galvanometer G indicates the absence of current, it is only necessary to multiply the number of millimetres $a\,d$ by 0·0002 to obtain the E.M.F. in volts. (For more details see Ostwald's *Physico-Chemical Measurements* [English Ed.], p. 210.)

Formulæ VI. and *VII.* indicate, what is confirmed by

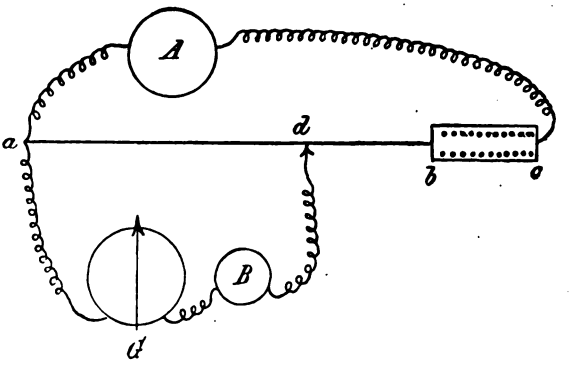


Fig. 35.

experiment, that π is essentially independent of the nature of the anions ; for instance, π is the same for the cells

$$Zn/ZnSO_4/CuSO_4/Cu$$

and

$$Zn/ZnN_2O_6/CuN_2O_6/Cu.$$

This phenomenon is made intelligible by the dissociation theory. The anion becomes important only when it very much decreases the solubility of the metallic salt. The formulæ referred to also show that the metal M_1 is the anode and M_2 is the kathode, provided the difference in brackets

emains positive. This condition is fulfilled as long as the alue of P_1 greatly exceeds that of P_2, and p_1 and p_2 do not liffer very much from one another.

These conditions are completely fulfilled by the Daniell ell which is now commonly used,

$$Zn/ZnSO_4/CuSO_4/Cu.$$

The E.M.F. of this cell amounts to 1·114 volts at 18°, with equimolecular solutions. This value must remain unchanged, according to the theory, provided the fraction p_1/p_2 maintains the same value, that is to say, provided the concentrations of the solutions are always equal. On the other hand, the E.M.F. must increase if the concentration of the zinc sulphate solution decreases compared with that of the copper sulphate solution. All these conclusions are completely confirmed by experiment, and they are easily understood, for the zinc must go into solution because its solution-pressure considerably exceeds that of the copper, and the passage of the zinc into solution takes place the more easily the fewer the number of zinc ions already present in the electrolyte; moreover, the copper ions must separate from the solution, and this process takes place more readily from a concentrated than from a dilute solution of a salt of copper. The deviations from the normal value of 1·114 volts are never very large. For even if the concentration of one solution is a thousandfold greater than that of the other, the difference amounts only to

$$\pm \frac{0{\cdot}0002}{2} 291 \log. 1000 = \pm 0{\cdot}087 \text{ volt.}$$

An especial theoretical interest attaches to the case wherein, in a zinc-copper cell, p_2 is infinitely small. In that case $\log. \frac{P_2}{p_2}$ must be greater than $\log. \frac{P_1}{p_1}$. The sign of π i reversed, that is to say, the current passes within the ce

from copper to zinc, so that the copper is the anode and the zinc the kathode. These conclusions are realised in practice when the electrolyte around the copper electrode is a solution of potassium cyanide. The electrodes K and A, of zinc and copper respectively, are fixed in the two limbs of an H-shaped tube, as shown in figure 36; the limb S_1 is filled to m with normal zinc sulphate solution (287 : 1000), and the limb S_2 is filled to n with normal potassium cyanide solution (65 : 1000); and a dilute solution of potassium sulphate, which serves as an indifferent conductor, is floated on the top of both solutions to the level $o\,p$. This cell causes a deviation of about fifteen degrees in the needle of the galvanometer G (figure 32), in the direction already indicated. On short-circuiting, little bubbles of hydrogen come off from A. After twenty-four hours, a zinc tree has formed from the upper end of K. The changes are somewhat as follows. The copper atoms pass into the solution of potassium cyanide, which is free from $Cu^{\cdot\cdot}$, in the form of ions, and are thus negatively charged. $Cu^{\cdot\cdot}Cy_2''$ is thus produced, while the free $K_2^{\cdot\cdot}$ travel to the SO_4'' anions of the potassium sulphate, and the $K_2^{\cdot\cdot}$ of this salt to the anions SO_4'' of the zinc sulphate, the zinc ions of which give up their charges to the zinc electrode that serves as kathode. The $Cu^{\cdot\cdot}Cy_2''$, however, reacts with $2K.Cy'$, whereby the charges are mutually neutralised, in accordance with the equation

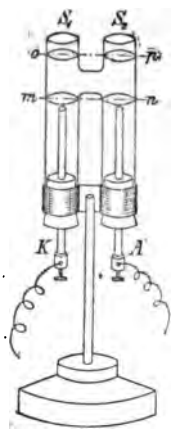


Fig. 36.

$$2K^{\cdot}Cy' + Cu^{\cdot\cdot}Cy_2'' = K_2^{\cdot\cdot}(CuCy_4)''.$$

As the copper passes into the complex anion $(CuCy_4)''$, it comes about that the electrolyte around the copper electrode is free from Cu; hence p_2 remains infinitely small.

Under the circumstances which generally obtain, log. p_1/p_2 may be put as = 0 without introducing a serious error. *Formula VII.* (p. 145) then takes this form:

$$\pi = \frac{0{\cdot}0002}{n} T \log. \frac{P_1}{P_2} \text{ volt} \quad \ldots\ldots\ldots \text{VIII.}$$

Hence, the E.M.F. of a Daniell cell is conditioned essentially only by the ratio of the solution-pressures of the metals; and the main process that occurs in the closed cell is that *atoms of the metal with the greater solution-pressure pass, as ions, into the surrounding electrolyte, while the kations of the second electrolyte discharge themselves on the second metal.* It follows that the first metal, that is, the metal that dissolves and to which the anions of its electrolyte approach, acts as anode, and that the second metal, whereon the kations of the electrolyte thereto appertaining separate in the neutral state, acts as kathode. Inasmuch as the conception formed by Nernst of the electrolytic solution-pressures of the metals must be analogous to that of osmotic pressure, because the experiments that have so far been made verify the calculations that are based on that analogy, it follows that the impelling force of a galvanic cell, by which quantities of electricity are set in motion, must have the character of a pressure-force. In this sense Ostwald rightly speaks of a galvanic cell as a machine which is worked by osmotic pressure (or electrolytic solution-pressure).

This way of looking at the matter is made clearer by the amalgam-cells of G. Meyer (*Zeit. für physik. Chemie*, 7, p. 477 [1891]). As the amalgams are solutions of metals in mercury, it is to be supposed that the tendency of the metals to ionise their atoms will increase proportionally to the c centrations of their amalgams. Amalgams in contact a solution of a salt of the metal in the amalgam

therefore give a current, the E.M.F. of which will be completely expressed by Equation VIII., as in this case $p_1 = p_2$. The measurements of G. Meyer agree extremely well with the theory. The mode of action of an amalgam-cell may be easily demonstrated by the cell represented in figure 37. The apparatus consists of two beakers, B_1 and B_2 (5 centims. high and 3 centims. diameter), which communicate by a tube, r, 1 centim. long and 2 centims. wide. The beakers are closed by caoutchouc covers with overlapping rims. The platinum wires a and h are fused into glass tubes and extend to the bottoms of the beakers. When 100 grams amalgam containing 1 gram zinc are placed in B_1, and 100 grams amalgam containing ·001 gram zinc in B_2, and the vessel is filled to above r with a solution, about 10 per cent., of zinc sulphate which has been made neutral by boiling with zinc carbonate, the galvanometer included in the circuit indicates the passage of a current from the dilute to the more concentrated amalgam, as is required by the theory. The E.M.F. at 15° is

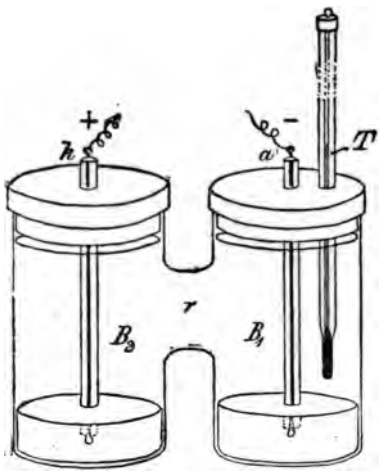


Fig. 37.

$$\pi = \frac{0{\cdot}0002}{2} \cdot 288 \cdot \log. \frac{1}{0{\cdot}01} = 0{\cdot}0576 \text{ volt.}$$

The needle, therefore, moves through 2·5 divisions of the scale. The effect of increasing the temperature may be established, very easily, by the same apparatus. It is only

necessary to place the beakers in a basin filled with hot water. When the temperature of the contents of the cell has risen to 60,° as read off on the thermometer T, the deviation of the needle becomes nearly twice as great as before. In accordance with *Formula VIII.*, the E.M.F. at 60° amounts to

$$\pi = \frac{0{\cdot}0002}{2} \cdot 333 \cdot \log. \frac{1}{0{\cdot}01} = 0{\cdot}0666 \text{ volt.}$$

Ostwald's definition of a galvanic cell as a machine driven by pressure suggests the use of an apparatus for conducting water, as represented in figure 38, for illustrating the origin and nature of the galvanic current. Although this analogy is not pertinent in every detail, nevertheless it is suitable for making clear the mutual relations of the magnitudes under consideration. The water-reservoirs A and K, and the pump P, represent the galvanic element; and the conducting tubes a b c d represent the connecting wire. If the flow of water is stopped by a stopcock at H, and the pump is kept at rest, the water attains the same level in the tubes r_{I}, r_{II}, and r_{III} as in K, just as the tension in the conducting wire is equal to that at the electrode when the circuit is open. But if the stopcock is opened, the water falls gradually in the tubes, as the tension in the conducting wire of a closed cell gradually decreases. The water flows at d into the reservoir A, which may be compared to the anode, and flows with the greater force the greater is the difference of level between the vessels K and A. The mechanical energy, that is, the product of the quantity of water flowing away and the force driving it, which force is determined by the height of the fall, corresponds. secondary conditions are neglected, with the avail electrical energy. Now, if the quantity of water flo

away in unit of time, which is comparable to the quantity of current, is to remain constant, the pump P must raise an equal quantity of water in unit of time into the vessel K, and consequently must work in such a way that the difference of level, which is analogous to the difference of potential, is not changed. The difference of level is primarily dependent on the height of the stand which supports the reservoir K, so that the height of the column of water above the point of overflow may be small in proportion to the height of the

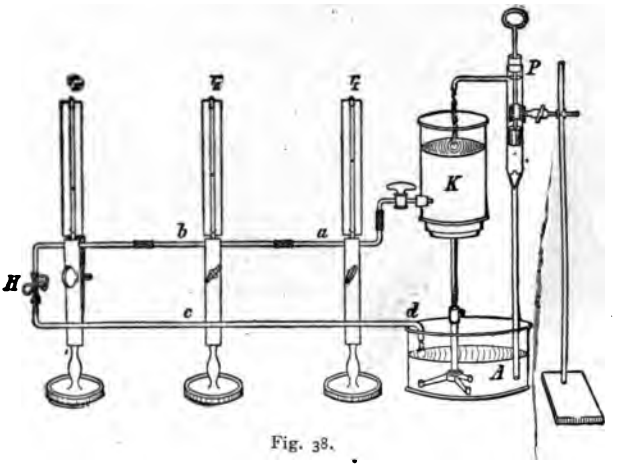


Fig. 38.

stand. The manner of working of the pump corresponds to the internal resistance of the cell. If the pump works freely, a greater quantity of water can be raised into the vessel K in unit of time than if the pump works with difficulty. In the latter case the outflow stopcock must be partly closed, just as strong currents cannot be obtained from cells with high internal resistances (compare Daniell cells, and lead accumulators). The quantity of water which flows away depends also, as the quantity of current depends, on the resistance in the conducting apparatus. The smaller the

cross-section of that apparatus the smaller will be the quantity of water that flows through it, the greater will be the energy which is lost because of the friction against the walls of the conducting tubes, and the more slowly will the pump have to work; just as a smaller amount of chemical change proceeds in an element which has a thin conducting wire. When the conducting tube has a large cross-section, the pump must work more rapidly in order to replace in K the quantity of water which flows into A; and in the analogous case, a greater quantity of chemical decomposition takes place in the substances which form a galvanic element. The resistance due to friction increases with an increase in the length of the conducting tube, and the quantity of water which flows away decreases. But the connection between the decrease in the quantity of water and the length of the tube is very complicated, whereas the quantity of current is simply inversely proportional to the length of the conducting wire. If liquids other than water are used in the apparatus represented in figure 38, other conditions being unchanged, the quantity of liquid which flows away is found to be dependent on the nature, and especially on the consistency, of the liquids, just as the specific resistances of the various metals are different.

[redacted]

[redacted] the result [redacted] that [redacted] in the [redacted] in which [redacted] trans-[redacted] of the nature of a pressure-force.

[redacted] that chemical processes occur in the [redacted] In the cell $Zn\,ZnSO_4\,CuSO_4\,Cu$ zinc is [redacted] zinc sulphate, and copper is precipitated from [redacted]hate. The material decomposition is expressed [redacted] zinc separates copper from the copper [redacted] valent quantity of zinc goes into solu-

tion. Whereas the chemical energy is transformed into heat when this change is caused to proceed directly by immersing a rod of zinc in a solution of copper sulphate, the chemical energy is transformed into electrical energy when the change takes place in a galvanic cell. Only in this case the process is an indirect one, in so far as it occurs in two phases at the two electrodes with the taking up and the abandonment of electrical charges ; thus

$$Zn + Zn^{\cdot\cdot}SO_4'' = Zn^{\cdot\cdot}SO_4'' + Zn^{\cdot\cdot}$$

and

$$Zn^{\cdot\cdot} + Cu^{\cdot\cdot}SO_4'' = Zn^{\cdot\cdot}SO_4'' + {}^{\cdot}Cu.$$

The process at the anode consists in an oxidation of the zinc by the anion SO_4''. The zinc itself acts as a reducing agent. The electrolyte of the kathode is reduced to copper ; it acts therefore, while the anion SO_4'' is available, as an oxidiser. The copper kathode remains chemically unchanged.

Ostwald drew especial attention to the fact that changes in the charges of the ions generally take place in all chemical processes that occur between electrolytic reducing and oxidising agents, and that these changes are a consequence of the different tendencies of the ions to take up or to give up further quantities of electricity. Moreover, he has proved that such an electromotive process can be brought about if the electrolytes are placed in separate vessels which are connected by an indifferent electrolyte, and electrodes on which these changes of charges can occur are present in the electrolyte. Platinum or carbon is a suitable material for the electrodes, because these are only required for the metallic conduction of the electricity, but do not themselves enter into any reaction with the electrolytes.

As such reduction- and oxidation-cells exhibit the t formation of chemical energy into electrical energy in a r

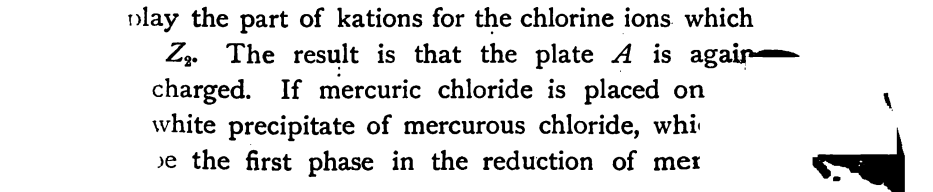
[illegible] is poured
[illegible] is nearly
[illegible] with the liquid an
[illegible] solution of stannous
[illegible] acts better : and an
[illegible] normal solution of
common salt (58·5 : 1000) is
poured into Z_2. The two cells
are connected by the syphon
filled with the solution of common salt. The
arms are about 3 centims. long ; they rest
[illegible] expansions of the cells d_1 and d_2
2 centim. apart. The needle of the galvano-
meter rests [illegible] as a few drops of chlorine
or bromine [illegible] are placed on the platinum
electrodes by means of a pipette, the needle
[illegible] which indicates that a current
[illegible] external circuit to A. The
[illegible] to the higher state of chlorina-
tion : two chlorine ions are required,

and two positive charges are also needed, to convert the divalent $Sn^{\cdot\cdot}$ into the tetravalent $Sn^{\cdot\cdot\cdot\cdot}$. Two chlorine ions are produced in Z_2 from one of the chlorine molecules placed therein, and the electrode K becomes positively charged. One $Sn^{\cdot\cdot}$ ion changes to a $Sn^{\cdot\cdot\cdot\cdot}$ ion by taking up two positive charges. By this means A is charged negatively The chlorine ions travel from Z_2 to Z_1. The process continues as long as molecules of chlorine are present on K. The change may be represented by the equation

$$Sn^{\cdot\cdot}Cl_2'' + Cl_2 = Sn^{\cdot\cdot\cdot\cdot}Cl_4'''',$$

which states that the reducer receives two positive charges, and the oxidiser two negative charges. The electrode of the former must, therefore, act as anode, and that of the latter as kathode, and the current must flow from the electrode of the oxidiser to the electrode of the reducer through the wire which closes the circuit. According to Bancroft (*Zeit. für physik. Chemie*, **10**, p. 387 [1892]), such a cell as that described has an E.M.F. of 1·171 volts.

Solutions of gold chloride and mercuric chloride act similarly to chlorine water; they place chlorine ions directly at the disposal of the stannous chloride, while the metallic ions strive to discharge themselves on the kathode. The gold forms a lustrous stain on the kathode. In these cases a solution of sulphur dioxide may be used as the reducing agent, and dilute sulphuric acid as the indifferent electrolyte. The sulphur dioxide is oxidised at the cost of the oxygen of



r, the two hydrogen atoms of which are ionised in
lay the part of kations for the chlorine ions which
Z_2. The result is that the plate A is again
charged. If mercuric chloride is placed on
white precipitate of mercurous chloride, whi
e the first phase in the reduction of mer

[illegible] plate [illegible] some sulphur [illegible] inasmuch as [illegible] concentrated solution [illegible] heat is applied [illegible] very instructive, [illegible] ferrous sulphate [illegible] sulphuric acid have been [illegible] solution of potassium [illegible] and touching the [illegible] with a crystal of potassium [illegible] sealing-wax to the end of a [illegible] the moment of touching the plate, the [illegible] The E.M.F. is 1·56 volt, according [illegible] The process is represented by the equation

$$[illegible] + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O.$$

The [illegible] of the two $KMnO_4$, by combining with the H_2 of the $10FeSO_4$ and with the $7H_2$ of the $7H_2SO_4$, forms eight molecules of water. In this way sixteen positive charges become available. Ten of these are conveyed through the connecting wire to the $5Fe_2$, which are thereby changed to ferric ions, and the remaining six positive charges go to the $2KMnO_4$, from which two Mn are produced, [illegible] two positive and two negative charges are neutralised.

Various cells may be constructed with the help of the apparatus shown in figure 39, wherein [illegible] may be gained by chemical processes which [illegible] ways to those already described. [illegible] precipitation of silver chloride in [illegible] equation

$$NaCl + AgNO_3 = [illegible]$$

produce electrical energy, [illegible]

the platinum discs of the electrodes A and K, the cell Z_1 is filled with a solution of common salt, and the cell Z_2, and also the syphon H, with an equimolecular solution of sodium nitrate. The galvanometer fails to detect any current from the cells as thus arranged; but the needle moves as soon as a crystal of silver nitrate is placed on the silver plate of the electrode K. The result is due to the passage into solution, in the cell Z_1, of silver ions from the silver plate, and to the separation of crystals of silver on the silver plate in the cell Z_2. Now, as only a small number of silver ions can exist in the solution of common salt, the silver plate in Z_1 is very quickly covered with a film of silver chloride, which darkens in the sunlight. This cell belongs to the class of reduction- and oxidation-cells; but it may also be regarded as a concentration-cell, because the concentrations of the silver ions are very different in Z_1 and Z_2.

According to Ostwald (*Naturw. Rdsch.*, **8**, p. 573), it is possible to transform into electrical energy the chemical energy that is set free in the neutralisation of sulphuric acid and potash. A normal solution of sulphuric acid is placed in the cell Z_2, and a half-normal solution of potassium sulphate in Z_1 and also in the syphon. If a piece of palladium foil about 4 sq. centims. area, that has been saturated, electrolytically, with hydrogen, is now laid on the platinum plate of the electrode A, and a st[illegible] of caustic potash is kept in contact with the pallad[illegible] for a short time, little bubbles of hydrogen rise [illegible] plate of the electro[illegible] the gal[illegible]eter indicates a power[illegible] from K to A. [illegible]pared palladium foil a[illegible] It is known tha[illegible] pall[illegible] properly [illegible]ling such lar[illegible] qu[illegible] hydr[illegible] the h[illegible] visibly wh[illegible] [illegible] short fro[illegible] burner. T[illegible]

[illegible] platinum like the metals possesses a certain [illegible] ionisation and while it becomes coated the electrode is negatively charged. The H ions thus produced react with the OH ions of the potash and combine with them to form neutral water, while the K ions travel to Z_2, where they impart the H ions of the sulphuric acid to become ionised at the electrode Z_2. The processes amount to the formation of water, as is also always the case in the formation of salts by the reactions of acids and bases; thus

$$2KOH + H_2SO_4 = K_2SO_4 + H_2O.$$

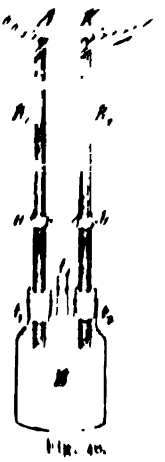


Fig. 46.

The peculiarity of the process in this cell is that the hydrogen which is required by the hydroxyl ions for the base for the formation of water is presented to them in the form of occluded hydrogen which must first be ionised at the anode. An extraordinary profusion of hydrogen is not required, inasmuch as the quantity of hydrogen which is used in Z_1 is obtained again in Z_2.

Ostwald classes the gas-cells, about the theory of [illegible] **ich there** has been much dispute, among reduc[illegible]tion-cells, and by so doing he gives a very s[illegible]n of the production of the curre[illegible]ydrogen-chlorine cell is the mos[illegible]40), which has a capacity of abou[illegible] with three tubuluses, t_1, t_2, and [illegible]st be narrow, in order that [illegible]istance between the two side[illegible], which are 20 centims. lo[illegible]buluses t_1 and t_2 [illegible]atinised *platinum*

foil* A and K are fused through the upper ends of R_1 and R_2. The whole apparatus is filled with dilute sulphuric acid. Electrolytic hydrogen is then allowed to accumulate in R_1 to the level a, by connecting A, as kathode, and a piece of platinum foil pushed through t_3, as anode, with the source of a current. The tube R_2 is then filled to b with chlorine. When the connecting wire from K is joined to that from A, a powerful current of 1·42 volts is obtained. A single gas element of this kind suffices to work a sensitive alarm-clock.

According to Ostwald, only those electrodes are suitable for gas-cells which are able to occlude gases. For it is only when it is occluded that a gas is in a condition to manifest its electrolytic solution-pressure, and this is especially the case with hydrogen. The current is produced in the hydrogen-chlorine cell exactly as the current is produced in the stannous chloride-chlorine cell which has been described already. Chlorine ions are readily formed in R_2 ($Cl_2 = 2Cl' + 80{,}200$ cals.), and by this means K becomes charged positively. These ions attract hydrogen ions from R_1, so that the occluded hydrogen in R_1 is obliged to form new ions. Hence the electrode A becomes charged negatively. While the current passes through the cell, equal

l chlorine disappear, as is required

en the cell is short-circuited, the

es R_1 and R_2 about 3 centims. in an

ll shows the smaller E.M.F. of

* cover it with finely-divided platinum,
position-cell containing a dilute solu
considerable quantity of hydrochlori
is used as anode. An accumulate
rent.

1·28 volts. The explanation of the origin of the current in this cell is somewhat more complicated. Each oxygen atom on the kathode side combines with two $H^{\cdot}$ ions, after these have given up their charges to K, to form water, and the available SO_4'' of the sulphuric acid causes the two atoms of occluded hydrogen of the anode tube to go into solution as ions, whereby the anode is charged negatively. Fresh quantities of hydrogen are occluded from the store of gas in proportion to the removal of the occluded hydrogen from the anode in the form of ions, and it thus comes about that the gaseous volumes of oxygen and hydrogen diminish in the proportion of 1 to 2.

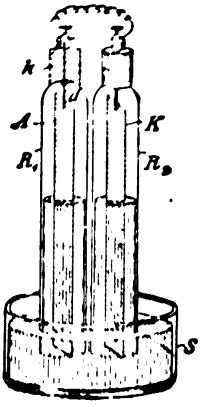


FIG. 41.

This theory of the hydrogen-oxygen cell is confirmed by the following arrangement. In figure 41, R_1 and R_2 are tubes 25 centims. long and 3 centims. wide: inside of these are placed the large platinised platinum plates A and K, to which are attached platinum wires, ·8 mm. thick, which pass through the tops of the tubes (R_1 and R_2) and are supported by corks; binding screws are ... ends of these wires. The tubes R_1 ... h a solution of potassium sulphate ...dded a little blue litmus solution in ...phenolph... in R_2; the tubes are ...ed solu... otassium sulphate, in ...t the ... parallel. The tubes ...ith ... hydrogen, respectively, ...s ...cted by a short wire. ...d the electrode A; if ...gain, the whole of the

liquid becomes red after about an hour; and a red zone, about 5 centims. wide, is seen at the top of the liquid in R_2. A free base has evidently been produced at K, and a free acid at A. Oxygen ions must be formed in R_2 which react with two potassium ions to form potassium oxide. The latter, being acted on by the water, changes to $K'(OH)'$, the two negative charges of the oxygen ion being distributed among the two $(OH)'$ [$K_2'' O'' + H_2O = 2\ K'(OH)'$]. Because of the excess of anions, the SO_4'' move from R_2 to R_1 where they cause the hydrogen to be ionised, so that the free acid appears in this tube.

Should the current of this cell not be sufficient to work an alarm-clock, which is a more suitable current-indicator than a galvanometer in a large hall, it is advisable to intercalate a relay including two dry elements, or to keep the tubulus t_3 firmly closed during the electrolytic charging of the cell. In the latter case the gases get compressed and they give the cell a greater E.M.F. (This is the principle of the gas-accumulators, which have not, however, yet obtained practical importance.)

More powerful effects are obtained by using the following battery (figure 42) than by employing a single gas-cell. Five holes are made on the longer side, l, of a rectangular t a distance of 15 mm. apart, and, alternating with ir holes are pierced on the opposite side, l'; platinum hich ar- soldered to platinum plates 43 × 47 mm. rough these holes, and the wires are two thick copper bars $a\ b$ and $c\ d$, means of loops of wire, in channeled ard. To prevent the displacement of plates, paraffin is poured on to th between these plates. The whol ed in a glass trough which is fille

onstant discharging current of 49 × 1·46 = 72 volts. It is of historical interest to note that this ingenious apparatus, which was based on the principle that is applied in the accumulators of to-day, was employed in the telegraphic service at Copenhagen.

Finally, this is the place to consider the problem suggested by Ostwald (*Elektrotechnische Zeit.*, **15**, p. 329 [1894]), as to how the chemical energy of carbon can be transformed directly into electrical energy. It is evident that the technical realisation of this idea, suggested by science, would be followed by consequences in comparison with which even the invention of the steam-engine would be thrown into the shade. For, on the one hand, electrical energy is that form of energy which is most easily and most completely exchangeable into other forms of energy; and, on the other hand, the enormous losses of energy would be avoided which are inherent in the methods now employed for producing electricity by dynamos driven by steam-power. The principle of Ostwald's "*element of the future*" has already been supplied by the gas-element. Generator-gas, as is produced by "gasifying" carbon, would have to be applied as the anode, and air as the kathode. Electricity would then be obtained by burning fuel, just as the chemical combination of hydrogen and oxygen is the cause of the ation of the current in the gas-element. The difficulty find suitable electrolytes, which shall not attack the or nd which shall themselves act only as an medium without thereby being exhausted. ing the attempts which have been made to n, it cannot be said that even the preliminary been accomplished.*

su experiments which have been made will be fou
fi *mie*, **4**, pp. 129 and 165 [1897].

CHAPTER V.

THE SOLUTION-PRESSURES OF THE METALS.

ACCORDING to Nernst's theory of current-production the E.M.F. of a Daniell cell with equimolecular electrolytes is expressed by *Formula VIII.* (p. 149); if this theory is to be tested by direct trials, it is necessary to find values for the solution-pressures, P, of the metals, by experiment. There is no great difficulty in arranging the metals in a series in the order of their solution-pressures. It is only needful to determine whether one metal is able to precipitate another from the solution of one of its salts, and hence, because of a greater solution-pressure, to draw away the electrical charges to the kations of the second metal. The following is the order for some of the well-known metals: zinc, cadmium, iron, lead, copper, mercury, silver. But it has not yet been found practicable to determine the values of P directly.

Nevertheless, it is possible to determine experimentally the difference of potential $\mathfrak{p}$ between a metal and the solution of one of its salts and, by the aid of the equation

$$\mathfrak{p} = \frac{\cdot 0002}{n} T \log. \frac{P}{p}$$

to calculate P,

$$P = p. \, 10^{\frac{n \cdot \mathfrak{p}}{\cdot 0002 \cdot T}} \quad \ldots\ldots\ldots \text{IX.}$$

The values of n, T, and p are given directly; and since an

electrode has been found, in recent years, which shows no difference of potential when compared with the electrolyte, the difficulties which before stood in the way of an empirical determination of $\mathfrak{p}$ have been overcome, at least in principle. Ostwald showed the way whereby this could be accomplished by demonstrating the behaviour of mercury dropping slowly from a capillary tube into dilute sulphuric acid.

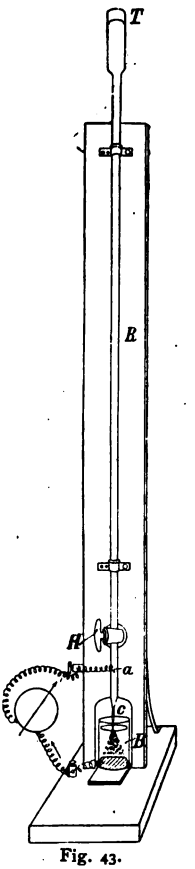


Fig. 43.

The following experiment will serve to indicate the method more fully. The glass tube R (figure 43), which is one metre long and 8 mm. diameter, is filled with mercury. This tube is provided with a funnel, T, a stopcock, H, a platinum wire, a, fused into the glass, and a piece of thermometer tubing, c, drawn to a capillary opening about $\frac{1}{3}$ mm. wide. The beaker B contains dilute sulphuric acid (1 : 3), the surface of which is about one centimetre from c, and mercury, with which a conducting wire is connected by means of a piece of platinum wire fused into the glass. When the stopcock H is opened, the stream of mercury which flows from the capillary opening divides itself into drops at one centimetre below c, and, although both electrodes are composed of the same metal, a current is detected, by the galvanometer, flowing from the wire which passes through the beaker.

According to the theory of Helmholtz, which is suppor by the experiments of Lippmann, the current is accou for by the relations between the electric potentials and

best determined by the compensation-method (p. 145). The difference $\pi - \cdot 56$ gives the potential-difference M/MS. The value $1 \cdot 10 - \cdot 56 = + \cdot 54$ volt was obtained for $\underset{\longrightarrow}{Zn/ZnSO_4}$ normal.

The difference of potential that has been most accurately determined, up to the present, is that between mercury and mercurous sulphate. The determination gave

$$\underset{\longrightarrow}{Hg/Hg_2SO_4} = - 0 \cdot 99 \text{ volt.}$$

From this value, and from the value of 1·514 volts found by Wright and Thompson for the E.M.F. of the cell $Zn/ZnSO_4/Hg_2SO_4/Hg$ at 18°, the following potential difference is deduced :—

$$\underset{\longrightarrow}{Zn/ZnSO_4} = 1 \cdot 514 - 0 \cdot 99 = + 0 \cdot 524 \text{ volt.}$$

This value is somewhat too large, as the zinc sulphate solution is only dissociated to 80 per cent. The value must be diminished by

$$^1/_2 \cdot \cdot 0002 \cdot 291 \cdot \log. \, ^{100}/_{80} = \cdot 003 \text{ volt,}$$

so that the corrected value $\mathfrak{p}$ is

$$\underset{\longrightarrow}{Zn/ZnSO_4} = + 0 \cdot 521 \text{ volt.}$$

By means of the dropping electrode, Paschen obtained the number 0·5187 when he used a solution of zinc sulphate that was twice normal, and the number 0·523, which comes very near to that given above, for a normal solution of the salt.

The E.M.F., at 18°, of the cell

$$Zn/ZnSO_4 \text{ normal}/CuSO_4 \text{ normal}/Cu$$

s been determined to be 1·10 volts; hence the difference of ential for

$$\underset{\longrightarrow}{CuSO_4 \text{ normal}/Cu} = 1 \cdot 10 - \cdot 521 = + 0 \cdot 579 \text{ volt.}$$

Hence the difference of potential for

$$\xrightarrow{\text{Cu/CuSO}_4 \text{ normal}} = -0{\cdot}579 \text{ volt};$$

that is to say, the electrolyte would have the potential of $-{\cdot}579$ volt if that of the copper were equal to zero. When the degree of dissociation of the electrolyte is taken into account, the more accurate value of $-{\cdot}582$ volt is substituted for $-{\cdot}579$ volt; and this value has been found by experiment, namely, by determining the E.M.F. of the cell

$$\text{Hg/Hg}_2\text{Cl}_2 \text{ dissolved in NaCl/CuSO}_4 \text{ normal/Cu.}$$

The differences of potential between the various metals and normal solutions of their salts can be calculated by subtracting from ·521 the empirically determined difference of potential of the cell $\text{Zn/ZnSO}_4\text{MSO}_4\text{/M}$.

In *Table XV.*, column *A* contains the composition of various Daniell cells arranged with equimolecular solutions, column *B* gives the E.M.F. of each of these cells as determined, at 18°, by the authors named in column *C*, and column *D* presents the calculated and corrected differences of potential, $\mathfrak{p}$, between the metals and normal solutions of their salts.

TABLE XV.

A.	B.	C.	D.
$\xrightarrow{\text{Zn/ZnSO}_4\text{/MgSO}_4\text{/Mg}}$	$-{\cdot}725$ volt	Wright and Thompson	$\xrightarrow{\text{Mg/MgSO}_4}$ $= +1{\cdot}243$ volt
$\text{Zn/ZnSO}_4\text{/CdSO}_4\text{/Cd}$	$+{\cdot}360$,,	F. Braun	Cd/CdSO_4 $= +0{\cdot}158$,,
$\text{Zn/ZnSO}_4\text{/FeSO}_4\text{/Fe}$	$+{\cdot}440$,,	F. Braun	Fe/FeSO_4 $= +0{\cdot}078$,,
$\text{Zn/ZnSO}_4\text{/Pb(C}_2\text{H}_3\text{O}_2)_2\text{/Pb}$	$+{\cdot}607$,,	Wright and Thompson	$\text{Pb/Pb(C}_2\text{H}_3\text{O}_2)_2 = -0{\cdot}089$,,
$\text{Zn/ZnSO}_4\text{/CuSO}_4\text{/Cu}$	$+1{\cdot}100$,,	F. Braun	Cu/CuSO_4 $= -0{\cdot}582$,,
$\text{Zn/ZnSO}_4\text{/Ag}_2\text{SO}_4\text{/Ag}_2$	$+1{\cdot}539$,,	Wright and Thompson	$\text{Ag}_2\text{/Ag}_2\text{SO}_4$ $= -1{\cdot}024$,,

The numbers in column D are characteristic magnitudes for the metals, provided that the temperature is taken as 18° and normal solutions of the salts are employed. The nature of the anion is generally unimportant, as this need be considered only when it greatly decreases the solubility of the salt. These values may indeed be liable to errors of a few hundredths of a volt, as they are all based on a single measurement, namely, that of the difference of potential between mercury and mercurous sulphate. But the discovery of methods of measurements which shall lead to more accurate determinations of the values of $\mathfrak{p}$ is only a matter of time. The equation for $\mathfrak{p}$ indicates that the sign of these values is determined by the relation of the values of P and p; hence, as $p = 22{\cdot}3$ atmos. for normal solutions, the sign is dependent only on P.

If the $\mathfrak{p}$-values of *Table XV.* are correct, the experimentally determined electromotive force, π, of a cell consisting of any two metals of the series in that table and their equimolecular salt-solutions must be equal to the difference of the $\mathfrak{p}$-values calculated for these metals. This conclusion is confirmed by experience. Streintz found, for the cell $Cd/CdSO_4/CuSO_4/Cu$

$$\pi = {\cdot}743 \text{ volt},$$

and the calculation gives

$$\pi = + {\cdot}158 + {\cdot}582 = {\cdot}740 \text{ volt}.$$

The observed value for the cell $Mg/MgSO_4/Ag_2SO_4/Ag_2$ is

$$\pi = 2{\cdot}212 \text{ volts};$$

calculated value is

$$\pi = + 1{\cdot}243 + 1{\cdot}012 = 2{\cdot}255 \text{ volts}.$$

ese agreements confirm the theory of Nernst, *accor*

to which the electromotive force of a cell has its origin in the places where the metals are in contact with their electrolytes.

The values for the solution-pressures of various metals given in *Table XVI.* are found by using *Formula IX.*, (p. 166), and inserting the empirically determined values of $\mathfrak{p}$.

TABLE XVI.

1	2	3	4
Metal.	Valency.	Solution-pressure, P, in atmospheres.	Weight, in grams, of metal in 1 litre of solution of the sulphate.
Mg	2	$0{\cdot}115 \cdot 10^{14}$	$1{\cdot}238 \cdot 10^{43}$
Zn	2	$1{\cdot}786 \cdot 10^{19}$	$0{\cdot}520 \cdot 10^{30}$
Cd	2	$0{\cdot}599 \cdot 10^{7}$	$3{\cdot}166 \cdot 10^{7}$
Fe	2	$1{\cdot}068 \cdot 10^{4}$	$2{\cdot}676 \cdot 10^{4}$
Pb	2	$1{\cdot}950 \cdot 10^{-9}$	$1{\cdot}805 \cdot 10^{-1}$
Cu	2	$2{\cdot}228 \cdot 10^{-19}$	$0{\cdot}313 \cdot 10^{-30}$
2Hg	1	$0{\cdot}223 \cdot 10^{-32}$	$0{\cdot}400 \cdot 10^{-31}$
2Ag	1	$0{\cdot}223 \cdot 10^{-33}$	$0{\cdot}216 \cdot 10^{-33}$

The values of the solution-pressures of the metals, with the exception of that of lead, are sometimes very great and sometimes very small; and, at the first glance, these values are difficult to understand. But when it is realised that the theory of Nernst represents the solution-pressure of a metal as the striving of the metal to overcome the opposing osmotic pressure of the kations which are already in solution, in order that the atoms of the metal may become ionised, then it is seen that the numbers in the third column express those osmotic pressures which the kations of the electrolyte must first possess in order that the ionisation may be impossible, and that the value of $\mathfrak{p}$ may be equal to zero. Now this would be the case if the quantities of the metals expressed, in

grams, in column 4, and calculated by means of the formula $p\ V = R\ T$, were contained in one litre of the solutions of the sulphates. But these quantities are either very large or very small, with the exception of that for lead, so that the gram-atomic weights of the metals (for mercury and silver the double atomic weights) present in one litre of the normal sulphate solutions either very much exceed, or very much fall short of, these quantities.

It follows, therefore, that the values of p must always be positive for the metals magnesium, zinc, cadmium, and iron, and always negative for the metals copper, mercury, and silver, even although the concentrations of the electrolytes vary within the possible limits. This will be intelligible if the character of an osmotic pressure is ascribed to the solution-pressures of the metals, and the theory of electrolytic dissociation is accepted, according to which the energy consumed in separating the molecule of the electrolyte into its ions does not enter into the consideration of the question. It will be understood that the electrolyte in which zinc is immersed assumes a positive potential, and the metal itself a negative potential, because the tendency of the zinc to convey positively charged ions to the electrolyte asserts itself. The reverse of this must, however, occur with copper, for the osmotic pressure of the copper ions of the electrolyte overcomes the solution-pressure of the copper. Hence the state of affairs is such that kations give up their positive charges to the copper, and the electrolyte maintains a negative potential. Now if the cell $Zn/ZnSO_4/CuSO_4/Cu$ is closed, the solution-pressure of the zinc and the osmotic pressure of the copper ions become permanently effective, and the result of this is that the electric current flows through the connecting wire from copper to zinc, from the kathode

metals

Neumann

TABLE XVIII.

1	2
$Zn/Zn(NO_3)_2/Cd(NO_3)_2/Cd$	+ 3
„ $/Pb(NO_3)_2/Pb$	+ 4
„ $/Cu(NO_3)_2/Cu$	+ 8
„ $/Ag_2(NO_3)_2/Ag_2$	+ 10
„ $/Mg(NO_3)_2/Mg$	− 2·5

If two different Daniell cells are arranged so that the kathode of one and the anode of the other consist of the same metal, and the cells are disposed one behind the other,

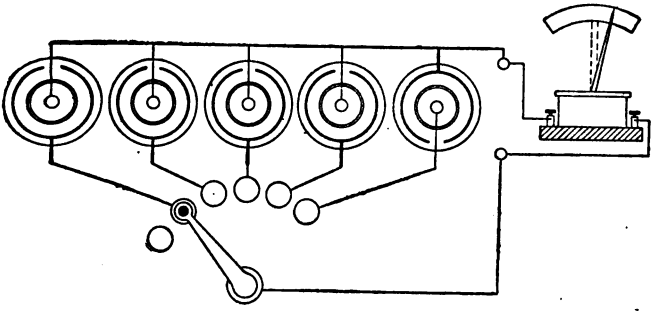


Fig. 45.

it is ...he expected that the total E.M.F. of the combination w ...ual to that of the cell which contains the anode ... he cells as anode, and the kathode of the other ... The value of π for the combination of cells ...SO_4/Cd and $Cd/CdSO_4/CuSO_4/Cu$ is calculated to ...

$$\cdot 521 - \cdot 158) + (\cdot 158 + \cdot 582) = 1 \cdot 103 \text{ volts},$$

and ...lue is found for the cell $Zn/ZnSO_4/CuSO_4/($ ...tive series of *Table XVIII.* arranges

It is therefore imperatively necessary to pay no regard to he older electromotive series; and this the more, because he production of electrical energy by the mere contact of wo substances is altogether against the law of the con- ervation of energy. Moreover, the old contact theory gave o explanation of the part played by the electrolyte in ne production of the current, nor did it indicate the ignificance of the chemical processes that occur in the ell.

As regards hydrogen, it is to be remarked that the general ehaviour of that element shows that it must be looked on s a metal, especially as large quantities of it can be taken p by certain metals, particularly by palladium,* and the roducts of these actions behave like alloys. Now, if a mall plate of palladium is saturated, electrolytically, with ydrogen, and is then immersed in a solution of copper ulphate, the plate is very soon covered with a lustrous ayer of copper. In a similar way, gold, platinum, silver, nd mercury are precipitated; but lead, iron, cadmium, zinc, nd magnesium are not precipitated.

The following facts are in accordance with these observa- ions: metals of the lead, iron, etc., class dissolve in acids with volution of hydrogen, whereas metals of the class which ontains gold, platinum, etc., do not evolve hydrogen from cids (overlooking such secondary reactions as those which ccur with nitric acid). Hence the value of the solution- re[illegible] of hydrogen occluded by palladium must lie between [illegible]he solution-pressures of copper and lead. Ex- [illegible]with a palladium-hydrogen plate and a normal [illegible] solution, at 17°, showed a difference [illegible] ual to − ·26 volt, putting the potential of t

* is capable of occluding 936 times its own volume

plate as zero; hence the solution-pressure of the hydrogen is calculated at $2{\cdot}414 \cdot 10^{-3}$ atmospheres.

It is to be expected that future researches in electro-chemistry will much extend the list of the values of p. These labours, which are reserved for the future, will not only contribute to the more exact extension of the new electro-chemical theory, but, as Ostwald insists, they will also be productive of fruit in the field of pure chemistry, in so far as they will make determinations of chemical affinity possible.

The more accurate knowledge of the electromotive series of metals in electrolytes has also very great practical interest. Wherever structures made of different metals, whether alloys, or combinations of different metals in contact, or metals which are encrusted with other metals mechanically or galvanoplastically, are exposed to the influence of substances precipitated from the atmosphere, there is a state of affairs suitable for the formation of short-circuited cells. In such cases one metal acts as the dissolving electrode and the other as the electrode which leads away the current. The former is therefore most exposed to destruction, while the latter is protected to a certain extent. An iron wire which has been covered with zinc does not rust so much at the places where the covering of zinc has been damaged as it would do were the layer of zinc removed entirely.

A few observations on the behaviour of iron towards tin may not be out of place here, without going into any minute details. A Daniell element, made of a small clay cell, with a cylinder of sheet iron and a fused rod of tin as electrodes, and having as electrolytes equimolecular solutions of the proto-chlorides of the two metals, as free as possible from acid, gives a deviation of the needle of the galvanometer which

:mains constant for several hours, in the direction which idicates that the iron is the dissolving electrode (the iode), and, as might be expected (*see* Neumann's electro-iemical series, p. 174), the rod of tin becomes covered ith a layer of spongy tin. But the E.M.F. of the :ment falls off immediately that hydrochloric acid added to the solution of stannous chloride. If 2 lumes of hydrochloric acid of specific gravity 1·124 : added to 16 volumes of this solution, the cell gives current, and if one volume more of the acid is added, : polarity of the cell is reversed and the tin becomes : anode.

This change of polarity may also be observed by im-rsing two equal-sized rods (7 mm. thick and 90 mm. long) annealed wrought iron and pure tin, which have been ished by wet quartz sand, in solutions of acids or salts concentrations of which range within certain limits. ure 47, p. 184, shows the arrangement. If solutions sulphuric or hydrochloric acid are used the strengths of ch vary from $^1/_{1000}$ to $^1/_{100}$ normal (·049 to ·49 gram SO_4, and ·0365 to ·365 gram HCl per litre), the iron as the kathode at the moment of the immersion of rod, but it becomes the anode when the cell has been wed to remain unclosed for ten to twenty minutes. If rmal acid solution is used, the iron acts as the electrode :h cts the current away, even when the cell is for twenty-four hours, and tin can be de-olution by mercuric chloride. The change marked in a half-normal solution of am-10 : 1000), for after one minute the needl e er moves in the opposite direction. a acts for a moment as the kathode, a di rds as the anode. If the electrodes

[illegible]

[illegible] iron and tin [illegible] series. The [illegible] of a single [illegible] may be [illegible] decided; [illegible] of the electrolytes have [illegible]

[illegible] is more liable to [illegible] than ordinary iron, is [illegible] of galvanic processes. [illegible] follows that the substances [illegible] must act as electrolytes [illegible] of iron and tin in such a way [illegible] the dissolving electrode. Salts of [illegible], and then decomposed with the [illegible]

experiments may serve to confirm this view. [illegible] figure 47 (p. 184) is filled with [illegible] When rods of iron and tin are [illegible] connected with the galvanometer [illegible] xygen and well-washed carbon [illegible] the water; the needle remains [illegible] ly 1 c.c. tenth-normal sodium [illegible] am NaCl), and 1 c.c. half-normal [illegible] = ·04 gram NH_4NO_3) are added, [illegible] shows itself to be the anode; [illegible] ned connected with the galvano-

meter for an hour, a thin yellow layer of rust is noticeable on the iron.

Again, if an iron-tin cell is filled with normal sodium chloride solution, and left short-circuited for thirteen hours, flocculent masses of rust are formed containing ·003 gram iron; whereas the rust which deposits in the same time, when the iron rod alone is placed in the liquid, contains only ·0018 gram iron.

As is well known, sheet iron is tinned to protect it from rusting; and these *tin plates* are used for making all sorts of domestic utensils. But if the layer of tin is damaged and the iron is laid bare rusting proceeds more rapidly and deeply at the exposed places than if the plates had not been tinned. If strips of tin are removed, by a knife, from a tin plate, exposure of the plate to moist air in summer for a couple of days suffices to produce red streaks of rust. But a plate of galvanised iron [that is, iron on which a coating of zinc has been deposited electrolytically] which has been treated in the same way shows no trace of rust.

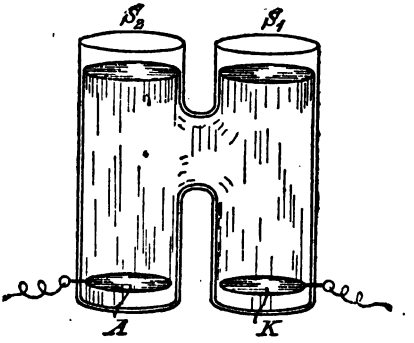
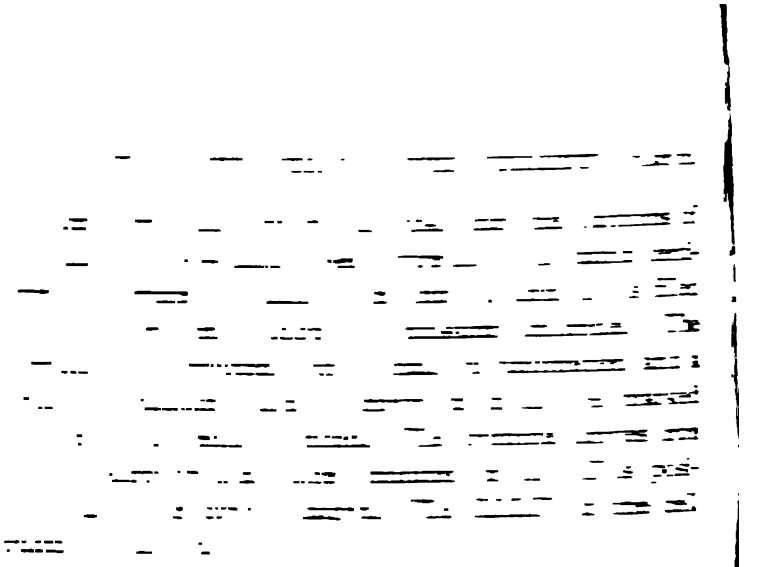


Fig. 46.

... of solution-pressures can be established for ...als whose atoms act as anions, and the values ...ces are connected with the chemical affinities ...als in question. The following experimer ... *Elektrochemie*, 4, p. 108 [1897]) shows tl ...eater tendency to ionise than iodine. T ... electrodes K and A are supported

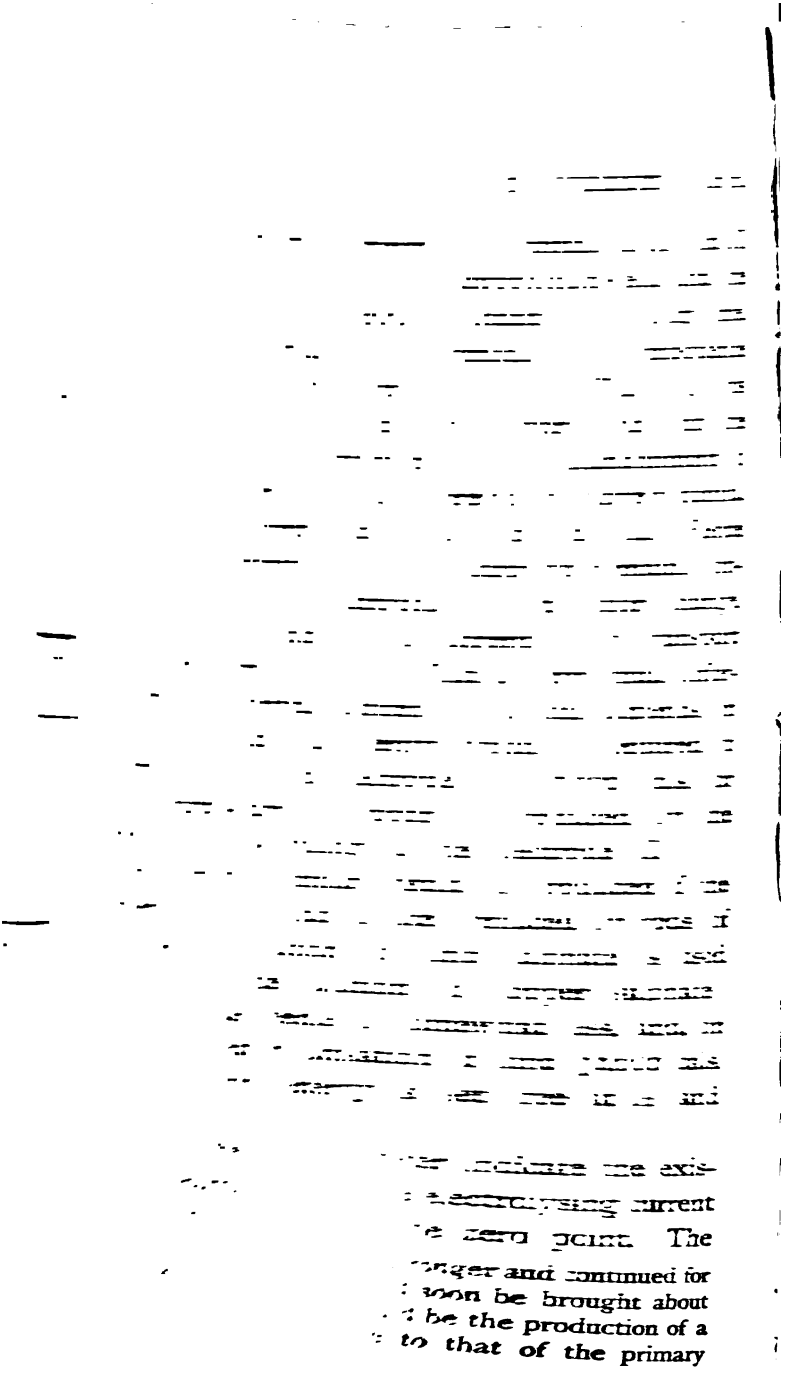


CHAPTER VI.

INTENSITY OF FIXATION AND POLARISATION.

THE results arrived at in the last chapter become of especial importance in that they afford information regarding the minimum electromotive force required for the electrolytic decomposition of a substance, and they also advance the comprehension of the phenomena of polarisation, regarding the theory of which there has been much uncertainty. When a current, whether it be such a current as is produced in a simple galvanic cell or one which flows through an electrolytic cell, causes changes in the electrolyte or on the electrodes, the current is always weakened; it is customary to refer this fact to polarisation.

Figure 47 represents an electrolytic cell filled with a normal ›lution of copper sulphate wherein two rods of copper, *A* ıd *K*, are immersed as electrodes. There is a difference of ›t on both electrodes, as against the electrolyte, of s :opper ions strive to separate on both. A ›ent may be constructed with a similar apparatus, lilute solution of sulphuric acid (1 : 20) and nc and iron. The E.M.F. of this cell is small; cing a resistance of about 1000 ohms, it The rod of copper *A* (figure 47) is he iron-pole, and the rod *K* with the ıometer is placed in the circuit. Not



electrodes show themselves to be *incapable of polarisation.* This phenomenon is always noticeable when a primary current does not bring about any changes of composition in the decomposition-cell, and hence when the direction in which the current passes is of no importance. The same conditions obtain in the Daniell cell, and, hence, the E.M.F. of that cell is constant, provided that considerable changes in the concentration of the electrolyte do not occur in consequence of the cell being kept in use for too long a time.

But the result is different when the electrodes are insoluble. If the electrodes are insoluble, between which the electrotysis of a salt of a heavy metal takes place, the gain or loss of energy which accompanies the separation of metallic ions on the kathode will not be made up for at the anode. Instead of the latter furnishing new kations, ions are disengaged there also, and these are anions. The separation of ions which occurs at both electrodes involves an expenditure of work, consequently the primary current suffers a greater decrease of electromotive force than that due only to the resistance of the electrolyte. This weakening of the primary current is called *polarisation.* It is to be referred to the greater or less tendency inherent in the particles to return to the ionic state [illegible] their electric charges are removed. Hence, a decomposition-cell with insoluble electrodes always shows a [illegible] or polarisation current, after the primary current [illegible] through it, and this secondary current flows in [illegible] that of the primary current.

[illegible] *sikal. Chemie,* **26,** p. 385 [1898]) has [illegible] all calorimetric measurements, the ex- [illegible] ired for the electrolytic decomposition [illegible] metals. The source of the curr[illegible] ement) was placed in an ice cal[illegible] , *c,* given out when the circuit [illegible]

closed was measured directly. The other part of the circuit consisted of a galvanometer, the decomposition-cell, and a resistance, r, so large that, in comparison therewith, the resistance of the cell might be neglected. The Joule-heat of the exterior portion of the circuit, c_1, was calculated, from the current-intensity, i, the magnitude, r, and the time of the experiment, t (always 3600 seconds), by the formula

$$c_1 = a\, i^2 r\, t \text{ cal.},$$

the heat-equivalent of one volt-ampère-second, a, being ·2362 cal. The total quantity of heat from the source of the current, C, was always referred to the same current-intensity of ·01 ampère, consequently to equivalent quantities of salts decomposed, so that

$$C = \cdot 01 \frac{c + c_1}{i} \text{ cal.}$$

The experiments were conducted both with non-polarisable electrodes and with polarisable electrodes (platinised platinum). The difference between the two quantities of heat, C, was 13·33 cals., at 0°, for a half-normal solution of copper sulphate. As this quantity of heat must be the equivalent of the current-energy used in the work of decomposition, it follows, from the equation

$$13 \cdot 33 = \cdot 01 \times \cdot 2362 \times \mathfrak{P}_0 \times 3600,$$

that the polarisation at 0° is

$$\mathfrak{P}_0 = 1 \cdot 57 \text{ volts.}$$

The value at 40° was found to be, $\mathfrak{P}_{40} = 1 \cdot 42$ volts; so that $\mathfrak{P}_{20}$ would amount to 1·48 volts for a normal solution of copper sulphate.

The term *decomposition-strain* of a salt has been given to the minimum value of that difference of potential which the

ıary current of a decomposition-cell must impart to insoluble electrodes in order to discharge the ions of both ls. The decomposition-strain will be indicated by the bol ℘; it has a definite value for each electrolyte. As : as the difference of potential does not reach the value no separation of the ions of the salt can occur; and, efore, the needle of a galvanometer inserted in the circuit ıins at the zero point. If the difference of potential, K, :ases beyond the value of ℘, the current-intensity, i, :ases, in accordance with the equation

$$K - ℘ = i\,w$$

ı w = the resistance of the decomposition-cell, and causes ıcreased separation of ions, in accordance with Faraday's provided care is taken that the ions are present in :ient quantity. The decomposition-strains determined by method agree exceedingly well with the calorimetric surements made by Jahn.

ı order to investigate more fully the character of the ıtity ℘, Le Blanc determined the individual values of the risation occurring at both electrodes, by throwing out primary current, at once combining the electrodes in tion with a normal electrode, and measuring electro- ically the potential-difference of the two. As regards the of the heavy metals, it was found that the (kathodic) ıs, p_k, were identical with the p-values of Neumann *VII.*). The individual metal-ions must therefore ıite force wherewith they strive to remain in the , that is, to hold fast the electric charges cor- h their valencies. This force, which is called *tion*, is therefore equal to the difference the metal, in the neutral state, exhibits electrolyte; and, consequently, it is to

ccording to Le Blanc's law, the decomposition-strains he electrolytes are definite quantities only when definite peratures and concentrations (or degrees of dissociation) assumed. The dependence of the $\mathfrak{p}$-value on these con-ons must be given by Nernst's formula

$$\mathfrak{p} = \frac{\cdot 0002}{n} \cdot T, \log. \frac{P}{p}.$$

investigations of Bose (*Zeit. für Elektrochemie*, **5**, p. 153 8]) satisfy this requirement as regards changes of concen-on. Under definite experimental conditions, Bose found decomposition-strains of $^1/_{10000}$ and $^1/_{100}$ normal silver ate solutions to be ·4845 and ·3682 volt, respectively; the rence between these numbers is ·1163. The arrangement he experiments was such that the values $\mathfrak{p}_a$ could not ergo any material change at the two concentrations; the rence of the $\mathfrak{p}$-values were caused only by differences in quantities $\mathfrak{p}_k$. Now, according to theory,

$$\begin{aligned} {}_{1/10000}\text{normal} - \mathfrak{p}_{k\,1/100}\text{normal} &= \cdot 0002 \cdot 293 \cdot (\log. 10000\,\mathfrak{P} - \log. 100\,\mathfrak{P}) \\ &= \cdot 002 \cdot 293 \cdot 2 \\ &= \cdot 1172 \text{ volt.} \end{aligned}$$

he value ·1172 volt agrees exceedingly well with the value 3 volt, which was found by experiment.

his example shows that the decomposition-strain in-onsiderably as dilution increases. The connection decomposition-strains and temperature will be in Part III., Chapter IX.

the results we have been discussing were obtained diture of much trouble and by using exceedingly ments, nevertheless they may be illustrated in the following simple lecture-experiment.

Z represents a decomposition-cell with fused-i

n connection with the foregoing experiment, it should be ticularly noticed that Le Blanc's law leads to the con- ision, that the difference of two decomposition-strains st be equal to the E.M.F. of a Daniell cell formed of respective salts and their metals. For, if 2·54 volts are uired to decompose a normal zinc sulphate solution at 20°, same E.M.F. must become available during the formation he zinc sulphate. The decomposition of normal copper phate solution, at 20°, requires the expenditure of 1·48 s. Hence, the E.M.F., π, of the zinc-copper cell must be $-1{\cdot}48=1{\cdot}06$ volts; and this is the value obtained by eriment. *Table XX.* contains data which confirm the clusion just stated. The very satisfactory agreement veen the calculated and the observed E.M.F. in each mple is a further proof of the justness of Le Blanc's ory.

TABLE XX.

Daniell cell.	π calculated.	π observed.
$Zn/ZnSO_4/CdSO_4/Cd$	·30	·360
$Zn/Zn(NO_3)_2/Pb(NO_3)_2/Pb$	·59	·500
$Zn/ZnSO_4/CuSO_4/Cu$	1·06	1·100
$Zn/ZnSO_4/Ag_2SO_4/Ag$	1·52	1·539
$Cd/CdSO_4/CuSO_4/Cu$	·76	·750
$Pb/Pb(NO_3)_2/Ag_2(NO_3)_2/Ag_2$	·93	·914
$Cu/Cu(NO_3)_2/Ag_2(NO_3)_2/Ag_2$	·46	·450

he results recorded in *Table XIX.* show that the anodic risation has the same value, namely, 2 volts, for sulphates nitrates. Taken as a whole, the results of the electrolysis alts of the stronger oxyacids give the same result. The tion of the cause of this phenomenon must find a rer from the investigations of the decomposition-stra cids.

The following experiment affords a preliminary survey of the subject. The cell Z (figure 50) is filled with dilute sulphuric acid, and is fitted with two polished platinum electrodes and the manometer M; the liquid in the manometer can be readily brought to the zero position by means of a three-way stopcock. E_1 and E_2 are two dry elements. The galvanometers G_1 and G_2 are placed in the primary and secondary circuits, respectively. The closing of the circuits is made by

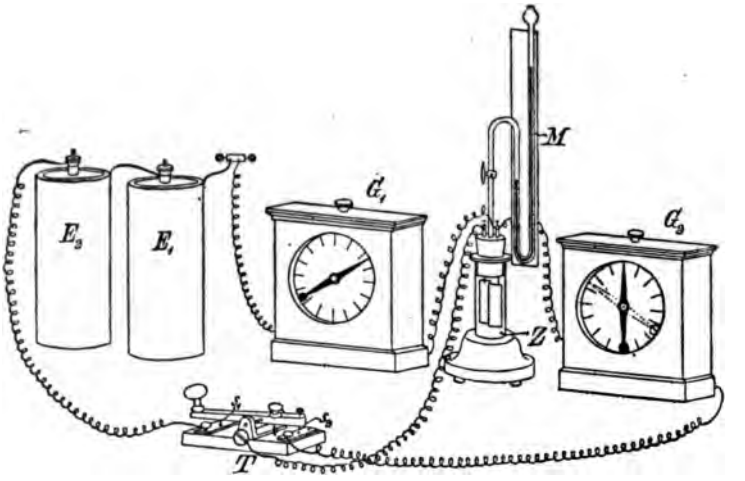


Fig. 50.

the Morse-key T. If contact is made with s_1, the electrolysing current is brought into action; if contact is made with s_2, the polarisation-current comes into play. If the primary current is from only one dry element, the needle of G_1, soon goes back to the zero-point; the polarisation-current also is of short duration. Gases are produced in Z only when two dry elements are used; the needle of G_1, shows a constant deflection, and the polarisation-current is stronger than before and lasts a longer time.

There are many differences between the statements con-
ning the tension required to produce gases in the electro-
ing acids. The experiments which have been made
licate that the material of the electrodes, and the intensity
the electrolysing current, effect the result, besides the
ıcentration and the temperature of the electrolyte. The
.tinised electrodes of Lummet and Kurlbaum seem to be
: most suitable. It must be supposed that a certain
ıount of work is necessary to press together the atoms, as
:y become neutral, into visible bubbles, and to remove them
m the neighbourhood of the electrodes. The finely-divided
.tinum on the electrodes referred to hastens the formation of
nute bubbles, and, therefore, the removal of the atoms, just
the presence of certain solid substances in a boiling liquid
ɜtens the formation of bubbles of vapour.

The mean value of 1·7 volts has been found for the decom-
ɜition-strain of oxyacids between platinised electrodes.
ın has shown that this number should be regarded only as
lower limit. For, the greater the number of discharged
ɜeous atoms formed as the current-intensity increases, the
ıre does the pressure on the electrodes increase, and this
reases the occlusion of the gases by the platinum-black,
l, therefore, impedes the removal of the gases ; this action
more marked in the case of hydrogen than in that of
ygen. Jahn (*Zeit. für physik. Chemie*, **26**, p. 385 [1898])
; expressed the relations between the current-intensity, i,
l the polarisation, $\mathfrak{P}$, which happens during the electrolysis
oxyacids between platinised electrodes, at 0° and 40°, by
following formulæ :—

$$\mathfrak{P}_0 = (2{\cdot}4033 + {\cdot}18452 \log. i) \text{ volts},$$
$$\mathfrak{P}_{40} = (2{\cdot}1320 + {\cdot}12605 \log. i) \text{ volts}.$$

These formulæ were obtained by reasoning on ce

ıe recent work of Glaser (*Zeit. für Elektrochemie*, **4**, 55, 373, 397, 424 [1898]), confirmed by Bose (*ibid.*, **5**, 53 [1898]), which has brought the problem nearer ion.

ıser started with the hypothesis that it *must* be possible ecompose dilute sulphuric acid, under certain experi- tal conditions, by an E.M.F. of 1·08 volts. He succeeded oing this by conducting the electrolysis between a large le saturated with oxygen, and a small kathode consisting ıe point of a platinum wire. He gradually increased the .F. to 1·08 volts; and then he observed, not only a ked deflection of the intercalated galvanometer, but also formation of minute gas-bubbles on the platinum wire. ɜn the E.M.F. was increased to 1·67 volts, there was a ked increase in the deflection of the needle, and a third iderable increase of the current-intensity occurred at volts. Glaser regards these three decomposition-points ıdicating that, in the first place, water is decomposed— rding to Küster, water contains not only $(OH)'$ but also ɣen ions, O''—by the discharging, at 1·08 volts, of the t the large anode by the $H^{\cdot}$ ions which are present in tity at the small kathode, and by the discharging of $(OH)'$ ions at 1·67 volts, and that the SO_4'' ions of the ıuric acid are discharged at 1·95 volts, because of the iency of the anions O'' and $(OH)'$. The neutral SO_4 must at once decompose to O and SO_3, and the bines with a molecule of water and produces

to this view, a primary decomposition of water ut the conditions for this decomposition are not illed; inasmuch as the O'' and $(OH)'$ ions ar oved because of the small degree of dissocia ınd the renewed dissociation of water occupie

a certain time, because it can proceed only to a very limited extent by reason of the presence of a very large number of hydrogen ions of the acid. The primary decomposition of water will precede the permanent electrolysis of the dilute sulphuric acid only for a short time, if the current-intensity is kept very small. If the latter rises, in accordance with Jahn's logarithmic formula, above ·0001 ampère, the polarisation for the normal sulphuric acid at 0° will exceed 1·67 volts, and the decomposition will be now confined almost entirely to the acid.

The numbers in *Table XIX.* (p. 188) show that the anodic polarisation during the electrolysis of oxysalts of heavy metals is independent of the nature of the anion; there is nothing extraordinary about this fact, inasmuch as the result, at the anode, of the action of the electric current is always merely a production of oxygen. But if this phenomenon is to be interpreted in the sense of the foregoing paragraphs, it is necessary to assume that the anions whose fixation-intensities are to be considered equal, must undergo changes corresponding with those of SO_4 ions.

However important the researches of Glaser and of Bose are with regard to the theory of the decomposition of water, and the processes in the hydrogen-oxygen cell, they do not lead to more than suggestions regarding the fixation-intensities of hydrogen ions and anions which contain oxygen. If it is assumed that the fixation-intensity of the hydrogen ion has the value −·26 volts (see p. 178), when water is decomposed with the minimum E.M.F. of 1·08 volts, then the fixation-intensity of O″ will be, according to Le Blanc's law, 1·08 + ·26 = 1·34 volts. This quantity is in keeping with the value of ·298 volt found, by Bose, for the decomposition-strain of normal silver nitrate solution, at 20°: if the fixation-intensity of the silver ion, namely +1·055 volts, is

acted, we get the number 1·35 volts. Moreover, the
num decomposition-strain of normal silver nitrate solution
volt, when polished platinum electrodes are used. The
ion-intensity of (OH)′ would then be ·7 + 1·055 = 1·755
s, and that of H· would be −·085 volt at the E.M.F. of
volts, whereat H· and (OH)′ are discharged, according
Glaser. Finally, if the value of 2·volts is maintained for
fixation-intensity of anions containing oxygen, H· would
e the fixation-intensity of +·05 volt
en dilute sulphuric acid is decomposed
an E.M.F. of 1·95 volts, and this value
uld increase, in the positive direction,
h increase of E.M.F. These numbers
fixation-intensities can be regarded
y as probable values.

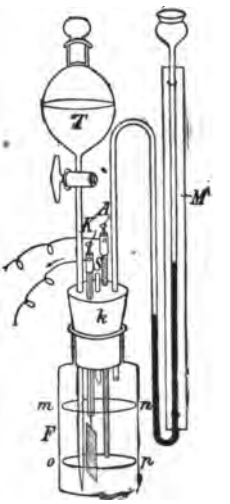


Fig. 51.

The following experiment demonstrates
fact that the fixation-intensity of
drogen ions, under ordinary conditions
pressure, is much smaller than that of
assium ions. The flask *F* (figure 51)
filled to the level *m n* with a dilute
ution of potassium sulphate. The
ctrodes *A* and *K*, made of zinc and
tinum respectively, are fastened through
cork *k* (this cork must fit firmly into the flask) in such
on that *A* dips about 2 centims. into the electrolyte
wholly immersed in the electrolyte. The cork *k*
the manometer-tube *M*, the stoppered funnel *T*,
nd of which is drawn to a fine opening and passes
n of the flask, and the piece of thin glass-rod *s*
hed into the cork after the apparatus has b

ately sensitive galvanometer is intercalated,

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331 EAST 10TH STREET,
CIRCULATING DEPARTMENT.

the circuit is closed, the needle shows a deviation which indicates the flow of a feeble current from K, but it soon returns to the zero point. A few atoms of zinc are sent into the electrolyte as ions, while a few hydrogen ions from the water give up their charges on the platinum. But as the number of these ions is very limited, and as the potassium ions, which have a very considerable, positive, intensity of fixation, do not give place to the zinc ions, the current very soon ceases. But if the glass rod s is withdrawn from the cork, and dilute sulphuric acid (coloured by indigo), of a specific gravity greater than that of the solution of potassium sulphate, is allowed to run from the stoppered funnel into the flask to about the level op, until the surface of the acid nearly touches the rod of zinc, the needle shows a much greater deviation. At the same time little bubbles of hydrogen rise from the platinum; and if the rod s is pushed into the cork, the liquid in the manometer-tube rises slowly. There is now a sufficient number of SO_4 ions available for the potassium ions; and the hydrogen ions of the sulphuric acid, the intensity of fixation of which is small, [illegible] proportion to the number of zinc ions which [illegible] Under these conditions the zinc continues to [illegible] the circuit is closed, although it is not in [illegible] the sulphuric acid.

It follows from the theory of [illegible] the heavy metals must be [illegible] mixture of several electr[illegible] [illegible] properties, pro[illegible] the ex[illegible] has the neces[illegible] [illegible] on either by [illegible] [illegible] is slightly exce[illegible] [illegible] to be decom[illegible] increasing the [illegible]

until a volt-meter included in the circuit indicates the proper E.M.F. The E.M.F. may exceed the required minimum to a certain extent, provided the kation to be separated, *k*, is present in large quantity, and it does not matter if it is not entirely removed from the electrolyte. For the electric current always does the smallest amount of work possible under the conditions. When the quantity of this kation falls below a certain limit, then the decomposition extends to the kations, *K*, which have the next greater fixation-intensity. In this case, the E.M.F. increases, while the current-intensity decreases. If it is desired to push further the separations of the kations, *K*, it is necessary correspondingly to increase the resistance of the external current-circuit, whereby the intensity of the current is further diminished. As aqueous solutions of electrolytes always contain hydrogen ions, whose fixation-intensity lies between that of copper and that of nickel, bubbles of hydrogen appear on the kathode when copper is almost completely precipitated; and more of these appear if the anode is insoluble, and, consequently, the quantity of free acid increases as the electrolysis proceeds. The presence of free acid in a mixture of electrolytes is, therefore, an excellent means for hindering the separation of ions of zinc, ...im, iron, ...l nickel, even when the E.M.F. is rapidly ... by ...ans, copper and silver can be separat... ...ly fr... four metals named.

The c... ...sity, ...n important factor in the ...oly... ...ration ...heavy metals; in scientific ...estig... current ... is usually referred to 0 sq... ...ims., an ... ...rk (D_2) to one square metre. ...de-s... ...sity is conditioned by th... ...ns of ...les ...les by E.M.F., a... ...ce' ...ath... ...rrounded on bo... sid... ...5 × ...tims., and ha...

therefore a total surface of 500 square centims., and let the current-intensity be 2 ampères; then, for this kathode, $D_1 = 4$, and $D_2 = 40$, ampères. If this kathode were replaced by another measuring 20 × 8 centims., then $D_1 = 625$ amperes, and $D_2 = 62{\cdot}5$ ampères, for the same current-intensity as before. Finally, if $D_1 = 1{\cdot}3$ when the current-intensity is 2 ampères, the kathode must have a surface of 154 square centims., in accordance with the equation $2.100\,x = 1{\cdot}3$, and must, therefore, measure approximately 12 × 6·4 square centims. The larger the kathode, the purer will be the metal of smaller fixation-intensity which is precipitated, and the easier, therefore, will be the separation of the metals one after another. On the other hand, if a small kathode is employed, the ions of one of the metals will soon be exhausted; then the E.M.F. will increase, if the source of the current permits this, and the metals of greater intensity-fixations will be precipitated. Even the metals of the alkaline earths may be separated at the kathode, from aqueous solutions of their chlorides, by using a current of great density. On the other hand, if a large anode is used, which con[illegible] several soluble metals, that metal wit[illegible] -pressure goes into solution most r[illegible] metals are dissolved simultaneously [illegible] If it is desired to separate the i[illegible] tensity as completely a[illegible]d as pure a[illegible] [illegible]es, large [illegible]odes may [illegible] stantly [illegible]en so[illegible] always [illegible]nt [illegible] f those [illegible]ns [illegible] een sent [illegible] must be

[illegible]y of the

metals precipitated on the kathode, but also the conditions of cohesion of these metals. The successful separation of the metals requires that the precipitate on the kathode should form a firm, coherent, layer; powdery or porous metallic masses soon fall off into the electrolyte and dissolve therein. This difficulty can be overcome, as a rule, by decreasing the density of the current. It depends on the nature of the electrolyte, also, whether the precipitate is or is not firm and coherent. The electrolyte must be made acid, or basic, and this or that acid, or base, must be used for the purpose, in accordance with the kind of metal which is to be separated. The object is sometimes attained by using such definite substances as change the kations into complex ions. Attention must also be paid to the temperature of the electrolyte.

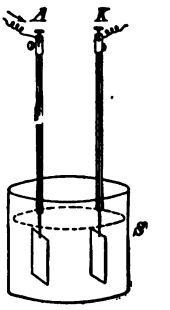


Fig. 52.

It is evident that many circumstances have to be taken into account in the electrolytic separation of metals. The following experiments make this clear.

Two solutions of sulphates, made perfectly neutral by boiling with the corresponding car[illegible] a placed in the cell *S* (figure 52); *the* [illegible]*ns* are 100 c.c. normal zinc sulphate, and 1 c.c nor[illegible]*per* sulphate. The platinum electrodes *A* and *K* [illegible] ims. in size, and are placed 3 centims. ap[illegible] is obtained from two accumulators. An [illegible]nce, and a large galvanometer, are pla[illegible] and a volt-meter is connected with the[illegible] the E.M.F. is 1·6 volts, a lustrous [illegible]ecipitated. After five minutes the [illegible]; the needle of the galvanome[illegible] the kathode is partially cove[illegible]gen. If the electrolyte is kep[illegible]

motion, by passing hydrogen through it, the needles of the volt-meter and the galvanometer return to their original positions and remain there for about 1½ hours, until the E.M.F. again increases. The bubbles of hydrogen constantly increase in number, on the kathode. Zinc is not precipitated, although there is now but little copper left in the solution, and the E.M.F. has risen to 2·5 volts. If the passage of hydrogen is stopped, the needle indicates 2·6 volts; precipitation of zinc begins on the kathode, and the deposit thereon takes the colour of brass; at 2·8 volts the deposit is grey, because only zinc is being deposited, in addition to hydrogen. Methyl orange added to the electrolyte, which is now colourless, becomes red, showing that much free acid has been formed. The phenomena which have been described may be caused to follow one another more rapidly by the following experiment. The vessel *G* (figure 53) is a flask the bottom of which has been cut off; a small disc of platinum (1·5 centims. diameter) fastened through the neck of this flask acts as anode *A*; the kathode consists of a platinum basin, *S*, about 8 centims. diameter, placed on the rim of the vessel *a b*; the current is led away from this basin by the wire attached to the binding screw *K*. This arrangement insures that the current-density gradually increases from the circumference of the kathode towards the centre, which is directly opposite the anode. The electrolyte consists of

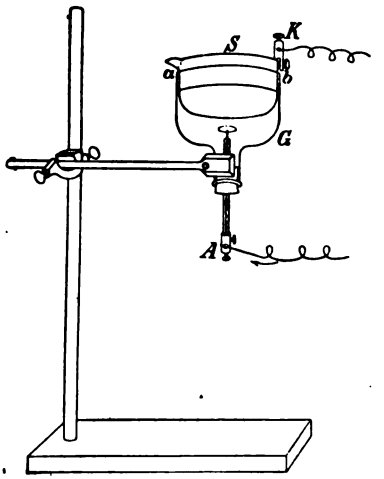


Fig. 53.

1000 grams water, 15·5 grams copper sulphate, 72 grams zinc sulphate, and 50 grams sulphuric acid. If the current from four accumulators is passed through a resistance of 50 to 60 ohms and then through the cell, that part of the platinum basin which is immersed in the liquid is soon covered with a lustrous layer of copper. When the resistance is removed a dull grey spot, about 3 to 4 centims. broad, appears opposite the anode; and if this spot is gently pressed with an agate pencil, it assumes a metallic lustre, and shows a white spot of zinc, in the centre, about 1 centim. broad, surrounded by a yellow ring of brass. Scarcely anything but zinc has separated exactly opposite the anode, because the current is stronger in the immediate neighbourhood of this position, and the small quantities of copper were already deposited. But the farther any particular part of the basin is from the anode the less is the tension, the greater is the number of copper ions still in solution, and the greater is the quantity of copper deposited thereon. Thus it comes about that the exterior ring of metal remains copper-red during the brief duration of the experiment, whereas the inner ring consists of copper and zinc which form brass when pressed ether.

e knowledge that the metals can be precipitated electro-lly one after another from a mixture of salts of heavy s has met with important applications. Metallurgical ists ploy electrolytic methods for the quantitative tals.* The electrolytic separation of metals more important in the refining of copper, traction of copper from its ores, for that l which makes it possible to obtain this quantities and purity for electrotechnical

Classen's *Quantitative chemische Analyse durch* Springer, 1892].

... The refining of the crude copper obtained by ... processes is conducted in baths of copper ... which are kept acid by sulphuric acid. Plates are ... for refining the crude copper, which may contain as ... per cent. of impurities, and these plates serve ... the kathodes are formed of thin sheets of pure ... immersed in the baths. The work of the current ... is obtained from dynamos, is merely to carry the ... from the anodes to the kathodes. The greater part ... the other substances that are contained in the crude ... is not dissolved by the anion SO_4, but falls down ... the anode in the form of a mud; this mud contains ... silver, gold, and platinum, besides copper sulphide, lead ... sulphate, and basic bismuth salts. The zinc and iron which ... into solution along with the copper are not precipitated on ... the kathode, because the tension does not exceed a certain ... maximum value. That the consumption of energy may be ... made as small as possible, the proper mixing of the baths ... must be attended to carefully; for loss of current is ... conditioned essentially only by the opposing force of the ... concentration currents (looking electrothermic action) ... which ... by an accumulation of the ... kati...

... Ti... ...nd Höpfner are used for the ... ...n its ores. The same principle ... processes ... e anode is made ... of ... conductor—lead ... ... diaphragm. The ... ... asted ores. The ... ...iefly on the fact ... ...ores which reduce ... ...ways occurs with ... ...the electrolysis

into a form wherein they are suitable for lixiviating fresh quantities of ore. Ferric sulphate, $Fe_2(SO_4)_3$, is used as a solvent in Siemens's method. This salt parts with an SO_4 group in the lixiviating vats, by which the CuS, Cu_2S, CuO, and Cu_2O in the ore are changed to sulphates; and the ferrous salt thus produced takes up an SO_4 group from the liquid surrounding the anode in the baths, in accordance with the equation

$$2FeSO_4 + SO_4 = Fe_2(SO_4)_3.$$

Höpfner employs a mixture of common salt and copper chloride solution for lixiviating the ores. Cuprous chloride is obtained in accordance with the equation

$$2CuCl_2 + Cu_2S = 4CuCl + S,$$

and this cuprous chloride remains in solution in the presence of the common salt. Copper chloride is re-formed in the neighbourhood of the anode, thus

$$2CuCl + Cl_2 = 2CuCl_2.$$

Höpfner's process has this great advantage, that, because of the monovalency of copper in cuprous chloride, the tity of metal precipitated in the baths is twice as great t which is obtained by the same current in the process mens.

ure 54 shows an experimental arrangement which repro- ant parts of the technical operations in this tion is made of 450 grams sodium chloride, stallised copper chloride, in 1500 c.c. water, uric acid, sp. grav. 1·18. This solution is n contact with copper shavings until it is en copper chloride is reduced to cupro on above), and the latter is dissolved um chloride. The anode, *A*, is a p

ised by the chlorine ions, so that copper chloride
d. The syphon H_1, which passes through a
e lower part of the vessel *Z*, serves to withdraw
om around the anode ; and the syphon H_2, which
osition by a cork placed in a hole in the plate
ws the liquid from around the kathode ; the
s withdrawn collect in *B*. About 20 c.c. of the
flow through the cell per minute. The green copper
olution flows from *B* into the vessel *C*, where it is in
ith copper shavings and dissolves copper ; in order
ate it with copper, the liquid must pass through
ow tube *c*, which is open at both ends, before it
into contact with the copper in the wider cylinder,
ess cuprous chloride solution drops into the flask *f*,
which it is transferred to *F*, and passes through the
where it gives up on the kathode the same quantity
pper as it dissolved in *C*.

e current from a battery of six accumulators passes to
nding screw, p_1, of the adjustable resistance* *W*. The
t passes from the binding screw p_2 through an ampère-
or, better, through an oxy-hydrogen voltameter, which
es the current, into the decomposition-cell, by *a*,
ives the cell by *k* to flow back to the battery. The
at the electrode is read off, every fifteen minutes, by a
ter, which is connected with *a* and *k* by the key *S* :
e key *s* is on the contact t_2, as in the figure, the volt-
in circuit.

olytic methods are in use for the refining of nickel,
silver, and gold.

sistance is arranged so that the three sets, from ·1 to ·9, fro
rom 10 to 90 ohms, can be thrown into, or removed from, t
eans of the three keys, w_1, w_2 and w_3. The apparatus
from Siemens & Halske, Charlottenburg ; price 150 mark

CHAPTER VII.

IRREVERSIBLE CELLS.

WHEN zinc is placed in an acid, along with an electrode which dissolves very slightly, or is altogether indifferent, and the circuit is closed, the greater solution-pressure of the zinc forces the hydrogen ions to discharge themselves at the indifferent electrode. The electricity is therefore led off from the electrode in question through the connecting wire. The current obtained from this cell is strongest immediately the cell is closed; but it soon decreases because of polarisation. For, on the one hand, the number of hydrogen ions of the electrolyte diminishes and the number of zinc ions increases; on the other hand, the internal resistance of the cell becomes greater, because the little bubbles of hydrogen adhere to the electrode which leads away the current; and, in the third place, an attraction comes into play between the adhering hydrogen and the anion of the electrolyte, whereby an electromotive force is produced which acts against the current.

The apparatus repesented in figure 55 serves for the more detailed examination of these occurrences. A cylindrical roll of pure zinc, Z, to which the rod of zinc A is screwed on, is placed at the bottom of the vessel G (6 × 18 centims.). C is a plate of copper, pierced with holes like a sieve, and bent so as to be concave on the lower surface. The little rods

copper s_1, s_2, s_3, and s_4 are riveted to the under surface, l the copper rod K to the upper surface, of the copper te. The vessel G is filled with dilute sulphuric acid 15), and is then firmly closed by the cork P, through ich pass the rods A and K, and also the exit-tube for s R. When A and K are connected by a wire which is so in connection with a moderately sensitive galvanometer, e deviation of the needle shows that K is the positive ole; and, whereas the liquid between Z and C remains lear, the liquid above C s turbid because of the ttle bubbles of hydrogen hich rise only from C. he gradual falling off of e current is shown by e slow return of the edle towards the zero nt, and also by the fact t the quantity of gas ing through R, and ected in a graduated ider, decreases in each d of five minutes.

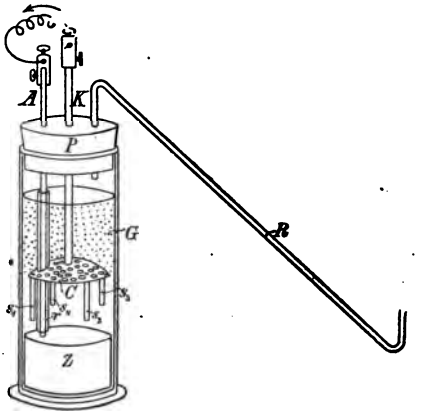


Fig. 55.

e internal resistance of the cell can be increased or ished considerably by raising or depressing the electrode ntact with A being prevented by the glass tube r gh which A passes; and in accordance with this change ernal resistance, the deviation of the needle, and the es of gas which come off (5 to 15 c.c. in each five s), vary also. One is able in this way to demonstrate pendence of the current strength on the resistance ned by Ohm's law, and also, although only approx the validity of Faraday's law within a source of

hydrogen on the zinc. This phenome-

ectrical endosmose, is due to the pressure
m the clay cell *T* into the space around
ore definite explanation has been given

currents are taken from cells the com-
ollows the type of the Daniell cell

$Zn/ZnSO_4/CuSO_4/Cu$,

es occur except that the concentrations of
vary somewhat by reason of the ionisation
d the un-ionisation of the copper ions. Cells
are unpolarisable, and their E.M.F. is *constant*.
e Daniell cells are *reversible*, inasmuch as if a
to the primary current is sent in the opposite
to such cells, no other action except the re-
nt of the original concentration is effected. On
hand, cells constructed like that described above,
/Cu, behave very differently. In these cells not
electrolyte, but also the electrode which conducts
current, is sensibly affected, in consequence of the
of the zinc and the disengagement of hydrogen.
cells are *inconstant and irreversible*. The original
f affairs is not restored by passing a current in the
ite direction into one of these cells. The E.M.F. of the
an no longer be ascertained by employing the equations
Nernst. Nevertheless, the general principles of the
eor can be applied to explain the production of
current from these cells.

nt cells may be made constant by preventing
of hydrogen at the electrode which conducts
rent. This is accomplished by oxidising th
ter, after it has given up its positive charg
, by such oxidising agents as chromic aci

lilute sulphuric acid (1 : 8) by the funnel *T*, the narrow ylinder *C* is filled with water and placed over the end of ıe tube *R*, and the conducting wires are then arranged in ıe manner shown in the figure. Under certain circumances it is necessary to connect a resistance coil, *W*, of ›out 500 ohms, with the galvanometer *G*. The galvanoeter can be thrown into, or out of, the circuit by placing e key of the commutator *U* in *a* or in *b*. If the key is t into *a*, the needle shows a deviation of about seven grees, but it soon returns some way towards zero. Small ›bles of hydrogen appear on *K*. If the key is now put › *b*, and the resistances of the galvanometer and the stance-coil are thereby cut out, so much gas is given off t about fifteen bubbles rise per minute in *C*. After a few utes the galvanometer is thrown into the circuit; the lle now moves through about five degrees only, because ›olarisation. About 15 c.c. of a concentrated aqueous tion of chromium trioxide (1 : 1) are now allowed to flow the point of the funnel *T*; this solution spreads through limbs of the cell, and the evolution of hydrogen at once s, because the hydrogen is oxidised with formation of and chromium oxide, which dissolves in the acid to chromium sulphate, as shown by the equation

$$2CrO_3 + 3H_2SO_4 + 3H_2 = Cr_2(SO_4)_3 + 6H_2O.$$

ıme time the needle very soon shows a deviation welve degrees; and the same deviation is shown circuiting for an hour and a half. After the cell ›ort-circuited for a couple of hours, the needle › the tenth mark on the scale, because of th up of the oxidiser, and considerable quantitie sulphate are now present in the electroly

[illegible]

[illegible] chromium [illegible]

[illegible] nitric [illegible] compounds of nitrogen. [illegible] and the [illegible] finally to [illegible]

[illegible] used as depolarisers [illegible] described [illegible] action of these [illegible]

[illegible] and sulphuric acid mixed [illegible] nascent hydrogen [illegible] these acids [illegible] While the [illegible] demonstrated in the limb con- [illegible] remains perfectly free from [illegible] which have been [illegible] detected in the acids that surround the

[illegible] changes which happen at the kathode in [illegible] cell may be thus expressed :

[illegible] $+ 6H = [illegible] - 3H_2O.$
$2H_2SO_4 [illegible] + 3H_2O$ . . . . . (A).

[illegible]ations [illegible]dicate the source of the high [illegible] vo[illegible] is given by the cell. The [illegible]renc[illegible] zinc and dilute sulphuric acid [illegible]'5 [illegible], great increase of potential can [illegible] m[illegible] discharging of hydrogen ions [illegible]de. [illegible]heory of reduction and oxidation [illegible] of the high E.M.F. (*Lehrbuch* [illegible] Part I., p. 892 [1893]). Three

atoms of oxygen disengage themselves from two molecules of chromic acid, and, reacting with four molecules of water, make felt their tendency to pass into the electrolyte as hydroxyl ions:

$$2H_2\cdot\cdot CrO_4'' + 4H_2O = 6(OH)' + 2Cr\cdots(OH)_3''' \quad \ldots\ldots (a).$$

But these hydroxyl ions exert a considerable attractive force on the hydrogen ions, which are driven into solution by zinc ions, and tend to neutralise these and produce water:

$$6(OH)' + 6H\cdot = 6H_2O \quad \ldots\ldots (b).$$

As equation (*a*) requires six negative charges in all, six positive charges will be conveyed into the circuit from the kathode, and that with a total pressure of 1·9 volts, for a potential increase of at least 1·4 volts will be obtained by the tendency of the oxygen to form hydroxyl ions. (Compare pp. 195, 196.) The chromium hydroxide of equation (*a*) will at once react with sulphuric acid to form chromium sulphate:

$$2Cr\cdots(OH)_3''' + 3H_2\cdot\cdot SO_4'' = Cr_2\cdots(SO_4)_3''' + 6H_2O \quad \ldots\ldots (c).$$

The sum of the equations (*a*), (*b*), and (*c*) gives the same result as equation (*A*); but the three equations give a satisfactory insight into the chargings of the ions, and explain the E.M.F. of the chromic acid cell.

tric acid in the cells of Bunsen and Grove

$$Zn/H_2SO_4 \text{ dilute}/HNO_3/Pt(C)$$

polariser, similarly to the chromic acid. Here
h E.M.F. of 1·9 volts, which is obtained by
cid of sp. grav. 1·33, is not to be accounted
a result of the oxidation of hydrogen io
of the nitric acid, but is to be attribut
of the oxygen to form hydroxyl ions.

As long as the nitric acid is present in quantity, the change proceeds in accordance with the equation

$$H \cdot NO_3' + H_2O = H \cdot NO_2' + 2(OH)'.$$

The nitric acid which is produced colours the depolariser green. The longer the depolariser is used the more does the E.M.F. decrease, for the less is the ability of the acid to give up oxygen, and the more must the hydrogen ions discharge themselves directly at the kathode; but, at a certain minimum concentration of the acid, the hydrogen no longer escapes as gas, but combines with nitrogen to form ammonia, which unites with a portion of the acid as yet unchanged. Thus

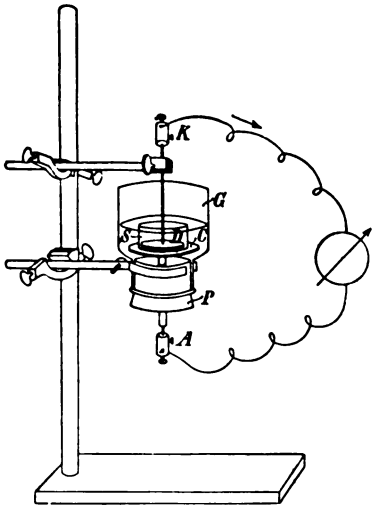


Fig. 58.

$$\begin{aligned} H \cdot NO_2' &= NO + (OH) \\ NO + H_2O &= N + 2(OH)' \\ N + 3H\cdots &= NH_3 \\ NH_3 + H \cdot NO_3' &= NH_4 . (NO_3)' \\ NH_3 + H . NO_2' &= NH_4 . (NO_2)'. \end{aligned}$$

Finally, bubbles of hydrogen appear on the kathode, and the E.M.F. of the cell now amounts to only about ·5 volt.*

The apparatus represented in figure 58 is arranged so that several oxidising agents may be brought into the electrolyte one after another, for the purpose of bringing about depolarisation at the kathode. The vessel *G* is fixed in the ring of a stand; the lower end of this vessel is closed by the cork *P*, through which passes the conducting

* This explanation is due to Ihle, *Zeit. für physik. Chemie*, **19**, p. 572 [1896].

d of the horizontally-placed copper disc *C*, which is ims. diameter. The small glass basin *S*, 3·5 centims. and 1 centim. high, rests on *C*; and the platinum), the conducting wire of which, *K*, is held vertically clamp, is placed on the bottom of this basin. When ssel *G* is so far filled with dilute sulphuric acid (1 : 20) he level of the acid is half a centim. above the rim little basin *S*, the needle of a galvanometer included circuit shows at first a deviation of about eight s; but in less than two minutes it swings back to ero point. On the other hand, as soon as small ties of the following oxidising agents are brought, fter the other, into contact with the platinum disc, edle shows a marked deviation, and very soon after nsumption, or the removal, of the oxidiser it returns zero point.

A little cube, 1 c.c. in size, formed of a mixture of carbon and *pyrolusite*, containing (as shown by iodometric analysis) 6·6 per cent. available oxygen, equal to 35·7 per cent. MnO_2.*

A cube of the same size cut from the peroxide plate of a Böse accumulator, containing 52 per cent. PbO_2 equal to 3·3 per cent. available oxygen.

A dilute solution of gold chloride placed on the platinum plate by means of a pipette; the gold is precipitated, after a few moments, as a lustrous deposit on the platinum plate.

Crystals of mercuric chloride, silver nitrate, and potassium permanganate; these crystals are fastened by means of wax on to glass rods, and are pressed on the platinum disc for a moment only.

* These may be obtained in prisms from Keiser & Schmidt, Philadelphia.

It is well known that solid oxidising agents, in the form of peroxides of manganese and lead, act as depolarisers in Leclanché cells, and in accumulators.

In the Leclanché cell

$$Zn/NH_4Cl/\underline{MnO_2\ (carbon)}$$

zinc is the dissolving electrode; and a concentrated solution of salammoniac is the electrolyte. The zinc dissolves in the salammoniac solution, with evolution of hydrogen, probably in accordance with the equation

$$Zn + 2NH_4Cl = ZnCl_2 . 2NH_3 + H_2.$$

This process may be demonstrated by adding a little water to a mixture of ammonium chloride and zinc dust, along with a small quantity of iron powder, in a gas-evolution flask, and collecting over water the gas which comes off in considerable quantity at the ordinary temperature. In the Leclanché cell the hydrogen is oxidised by the manganese peroxide in the carbon cylinder:

$$H_2 + 2MnO_2 = H_2O + Mn_2O_3.$$

In order to recognise the depolarising effect of manganese peroxide by an experiment specially arranged for that purpose, a piece of platinum foil, *A* (figure 59), and a prism of carbon and manganese peroxide (having the same composition as the cube already described) are placed in the limbs of a Hofmann's U-tube; and the apparatus is filled with dilute sulphuric acid (1 : 12). When a current is led into the apparatus, oxygen is given off at *A*, but no hydrogen rises from *K* provided the current is weakened sufficiently by a resistance intercalated into the circuit.

is experiment the hydrogen ions are oxidised by anganese peroxide after they have been discharged, as happens in the Leclanché cell. If the current is stronger, some hydrogen collects in the kathode-; but the volume of the hydrogen is always less than the volume of the oxygen which collects in the -limb.

e power of depolarisation of a mass of n and manganese peroxide is evidently er the stronger the current may be which causes evolution of bubbles of hydrogen, is, which polarises the kathode. In order st the capabilities of rods of carbon and anese peroxide containing different quan- of the peroxide, a water voltameter (of J-form devised by Hofmann), with two num electrodes, a galvanometer, and an table resistance, were included in the it of the apparatus represented in figure By means of the galvanometer and the ance, it was possible to maintain the nt at a constant intensity for a long

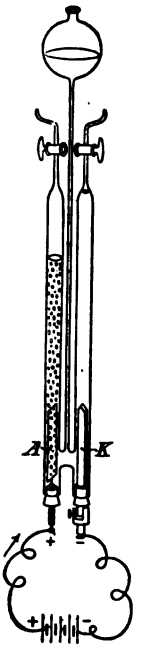


Fig. 59.

Table XXI. gives a synopsis of the s of the measurements, and makes the of working of a Leclanché element ble.

mbers in columns 2, 5, 8, and 11 show that the g effect of a kathode of carbon and manganese creases with increase of the quantity of peroxide, e one increase is not directly proportional d that this effect gradually diminishes aft n in used for a long time. The fact i that the Leclanché element gives a cc

			per cent. H
			per cent. H
			per cent. H

...ture rise of a short time, but that after a longer time ...ed the more easily the less the quantity ...anese peroxide it contains. As the cylinders of ...n and peroxide in the elements that are used in the German Imperial telegraphic service contain, on the average, only 15 per cent. MnO_2, the current that is taken from ...ed 0·07 ampères. If a stronger ... cells must be arranged parallel ...n which is sometimes expressed ...oxide of the carbon kathode is ... erroneous, inasmuch ... has no depolarising

...show that the volume ...atus continues to be ...meter. This is ex- ...anese sulphate which ... the anode-limb

TABLE XXI.

6	7	8	9	10	11
With the same current of 0·072 ampère there were evolved in the following 25 minutes			In the next 75 minutes, until polarisation began, there were evolved		
in the voltameter	in the experimental apparatus	hence the MnO_2 fixed	in the voltameter	in the experimental apparatus	by a current of
12·84 c.c. H 6·42 c.c. O	4·60 c.c. H 6·19 c.c. O	61·06 per cent. H	9·40 c.c. H 4·70 c.c. O	0·50 c.c. H 4·30 c.c. O	·018 amp.
13·98 c.c. H 6·99 c.c. O	4·47 c.c. H 6·35 c.c. O	68·03 per cent. H	12·86 c.c. H 6·43 c.c. O	0·69 c.c. H 5·52 c.c. O	·024 amp.
12·90 c.c. H 6·45 c.c. O	0 c.c. H 6·36 c.c. O	100·00 per cent. H	18·38 c.c. H 9·19 c.c. O	0·92 c.c. H 8·96 c.c. O	·035 amp.

and is there oxidised to $Mn_2(SO_4)_3$ or to some higher oxidised compound; for, as a matter of fact, the electrolyte near the anode soon assumes a rose-red coloration.

CHAPTER VIII.

ACCUMULATORS.

THE depolarising action of lead peroxide is much more effective than that of carbon-manganese peroxide; a mass of the former compound conducts the current metallically. Let a Hofmann's apparatus for the decomposition of water, and two apparatuses constructed in the manner shown in figure 59, be included in the circuit of a battery of twenty accumulators. The kathode of one of the two apparatuses is a prism of carbon-manganese peroxide containing 35·7 per cent. MnO_2, which is equivalent to 6·6 per cent. available oxygen; the kathode of the other apparatus is a prism cut from the lead peroxide plate of a Böse accumulator containing 51·8 per cent. PbO_2, which is equivalent to 3·3 per cent. available oxygen. After twelve minutes 62 c.c. hydrogen have come off from the platinum kathode of the apparatus for decomposing water, and 41 c.c. hydrogen from the carbon-manganese peroxide kathode. But the limb that contains the kathode of lead peroxide remains quite free from gas. The reason of this behaviour is found partly in the structures of the two oxidising agents, for the mass of lead peroxide is much less dense than that of the carbon-manganese peroxide, and there are, therefore, many more points where the hydrogen ions are attacked by the oxidiser, and partly in the different rates of reacti

lead peroxide gives off oxyen more easily than manese peroxide, as may be seen by heating the two ›stances in test-tubes. Whereas such a prism of carbon-.nganese peroxide is polarised by a current of 0·063 ıpères, the lead peroxide is able to sustain a current of ur ampères without hydrogen being set free, that is, ithout the E.M.F. of the accumulator being weakened by olarisation. This is, generally, the maximum quantity of urrent which can be taken from an accumulator that ontains a single peroxide plate, and if greater quantities ›f current are required, several cells must be arranged parallel to one another. The extraordinarily great depolarising action of lead peroxide explains why accumulators are so superior in steadiness even to Bunsen cells.

The foregoing experiment elucidates the processes which take place at the peroxide plate during the discharge of an accumulator, for the hydrogen is carried to that plate in the ionic state. The changes may be represented briefly by the equation

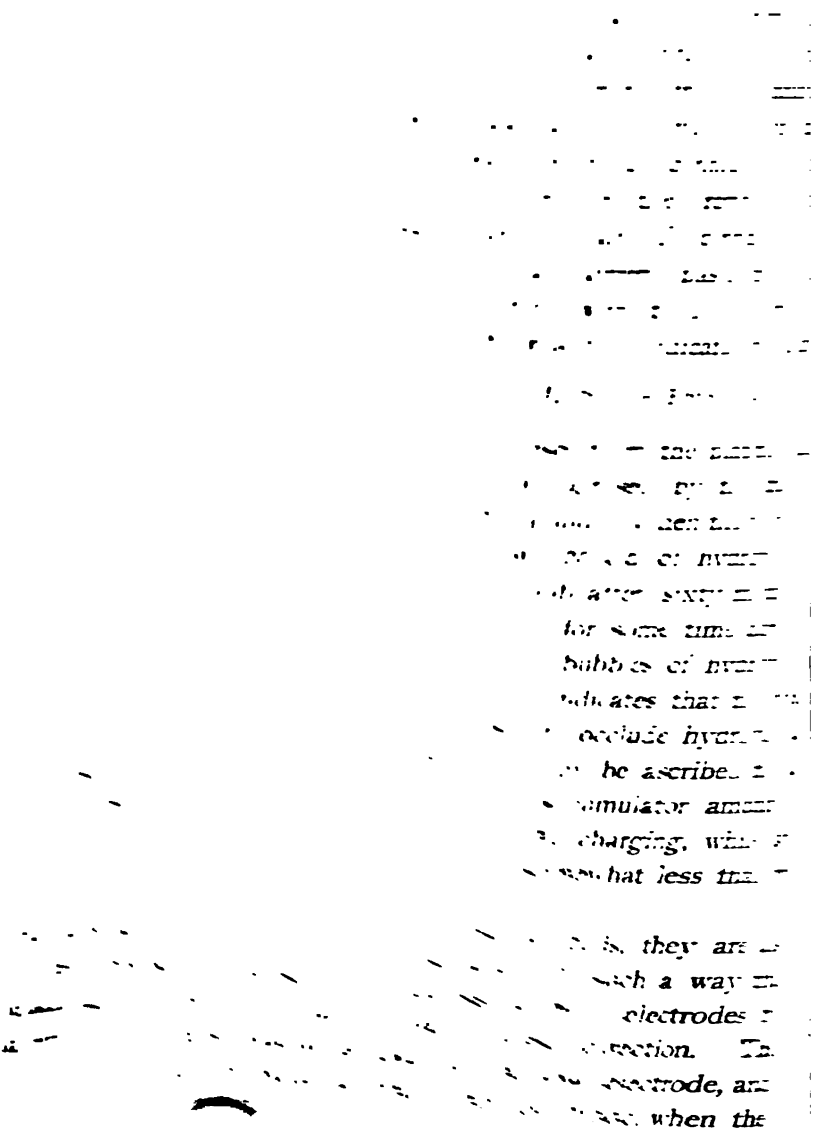
$$PbO_2'' + H_2'' = H_2O + PbO,$$

and the sulphuric acid then reacts on the lead oxide in accordance with the equation

$$PbO + H_2''SO_4'' = H_2O + Pb''SO_4''.$$

processes that take place at the peroxide plate may nonstrated by the use of a Hofmann's U-tube. In 6c 4 represents a prism cut from the lead plate of a atcr,* and K is a platinum electrode. Dilute

p ism (which is certainly very brittle) is not to be had, f lead may be cast, and the surface increased by channels. Before the experiment, the outer layer › a spongy mass of lead by repeated oxida' ofmann's U-tube by Planté's method. The res' is treatment, the channels are filled with a ed lead with sulphuric acid.



lowing experiment illustrates the charging of an
:or, and especially the production of the accumulator
)lder Planté's method, the principle of which is
arted from in any essential respects in the more
rocesses. Figure 61 represents a glass trough which
with dilute sulphuric acid (1 : 4). The leaden plates
and P_3, which have been cleaned very carefully with
made of steel wires, are placed in the channels of the
side-walls of the trough in
way that they can be lifted
asily. As thus arranged the
of course, gives no current.
lates P_2 and P_3 are connected
)ne another; and the negative
of a battery of at least two
ulators is connected with these
by means of the binding screw
he positive pole of the battery
nected with the plate P_1 by
inding screw *a*. When the
e of the current into the cell
en continued for about twenty
es, both sides of the plate P_1
become covered with a dark brown layer of peroxide;
as the plates P_2 and P_3 appear dull grey, in consequence
reduction of the oxide present upon them, and also
e of the occlusion of hydrogen which has taken place
e extent. The current which can be obtained from the
en after that short period of charging, is strong enough
an alarm-clock in action; it even suffices to decompose
su[illegible] acid. If at least three cells, such as th
1, are prepared, and if they are charged
l times, it can be shown that the quan

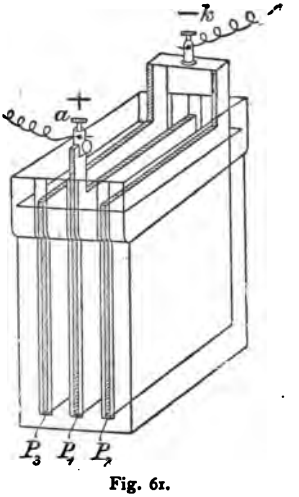


Fig. 61.

of current obtained from them gradually increases. The volumes of gas, for instance, which are produced by discharging the cells through a water-voltameter, or the number of minutes which the current is able to keep alight an incandescent lamp (of about five volts), increase the more the more often the charging and discharging of the cells is performed.

If it is desired to charge a few accumulators obtained from the manufacturer for experimental use, or for some special practical purpose, and if neither the current from a dynamo nor a Gülcher's thermopile is at hand, the copper elements used in the [German] Imperial telegraphic service may be employed. These are constructed on the principle of the Meidinger cell, in the manner shown in figure 62. The vessel, *g*, of one litre capacity, contains a thick-walled ring of zinc, *Zn*, which acts as the anode, and which is suspended from the rim of the vessel by three strips of zinc. The leaden plate *P*, into which is cast the rod of lead *s*, acts as the kathode. The vessel is filled with water, in which about 20 grams of zinc sulphate are dissolved, and about 100 grams of crystals of copper sulphate are placed on the bottom of the vessel. A number of such cells are arranged in a proper way to form a battery, which is fixed in a frame and kept at rest, so that the mixing of the salt solutions may be avoided as far as possible. The E.M.F. of a copper element of this kind is one volt after a few hours; it remains constant for several weeks, and then diminishes to 0·95 volt. The internal resist-

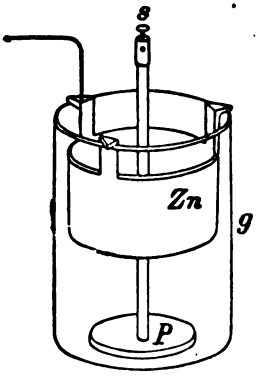


Fig. 62.

nounts to from three to eight ohms according to the
:rations of the solutions. Although the intensity of the
is small, yet it varies within very narrow limits even
:ourse of several months; and it is only necessary to
›re or less copper sulphate to insure the proper working
cell. The rings of zinc last for a long time. The
of copper elements is
:ed, by a switch, with
:umulators that are to be
l; and after the current
he accumulators has been
the battery is switched
:ain and re-charging is
l.

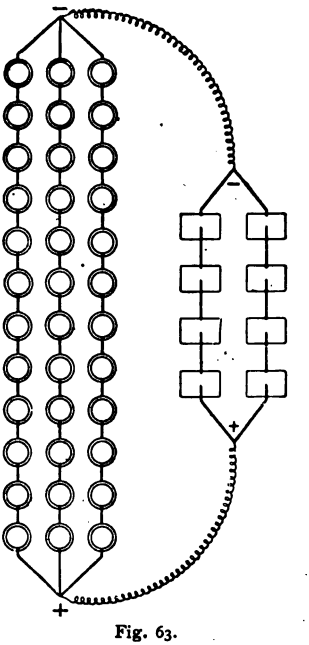


Fig. 63.

following example may
› show how the connection
a charging battery with a
of accumulators can be
lished. It is required to
eight accumulators by the
thirty-six copper elements.
copper elements are
d in series behind one
the three parallel
ined. The eight
connected in two rows of four in each,
bi :d rows parallel to one another, and
ging battery are connected in the
63.
ne copper element is 1 volt, and
is 5 ohms, and if the opposin
:tor is 2·2 volts, then, neglec
resistance of the accumulat

the intensity of the current from the charging battery is

$$i = \frac{(12 - [2{\cdot}2 \times 4])\,36}{5 \times 12^2} = {\cdot}16 \text{ ampère.}$$

Now if the capacity of an accumulator amounts to 40 ampère-hours, then 80 ampère-hours must be obtained from the charging battery, because of the parallel combination of the two rows of accumulators. Hence the battery of accumulators will be charged in $80/0{\cdot}16 = 500$ hours. This example shows that the accumulators are storage-machines in the true sense of the word; for the electrical energy which gradually collects in them can be drawn off when required, either in small quantities or in large quantities, which may amount to 72 volt-ampères in the foregoing case, at least for a short time. Moreover, as 1 ampère separates 1·181 grams copper in one hour, and hence consumes 4·651 grams crystallised copper sulphate, and 1·213 grams zinc, the charging battery uses $3 \times 80/3 \times 12 \times {\cdot}004651 = 4{\cdot}5$ kilos. copper sulphate, and 1·2 kilos, zinc, during the process of charging, in the example given.

Let m = the number of copper elements;
e = the E.M.F. of one of these elements;
w = the internal resistance of one of the copper elements;
p = the number of copper elements combined in series (in one of the rows);
n = the number of accumulator cells;
π = the opposing E.M.F. of one of these accumulators;
q = the number of accumulator cells combined in series (in one of the rows);

then, neglecting the internal resistance of the accumulator

the battery of accumulators will be charged by a current
: intensity

$$i = \frac{(e\,p - \pi\,q)\,m}{w\,p^2} \text{ ampères.}$$

let an accumulator cell have the capacity of C am-
ıours; the charging current must supply $C \,.\, n/q$ ampère-
. Putting t as the number of hours required for
ing, then—

$$i\,t = C.\,\frac{n}{q};$$

—

$$t = C.\,\frac{n\,w}{m} \,.\, \frac{p^2}{q(e\,p - \pi\,q)} \text{ hours.}$$

this it follows that, when C, n, w, m, e, and π remain
ınt, t has a minimum value when

$$p = \frac{2\,\pi}{e} \,.\, q,$$

ı this case,

$$t = C.\,\frac{n\,w}{m} \,.\, \frac{4\,\pi}{e^2}.$$

:, in order to charge as quickly as possible, the number
ırging elements arranged in series ought to be about
ınd a half times the number of accumulator cells
:ed in series in one of the rows.
:hould be remarked, in regard to the zero effect of
ulators ''at a distinction must be made between the
ty lo t(be obtained from the accumulator,
is in ampère-hours, and is dependent on
substance—the "active mass"—
le, and the available energy of
rr .d in watt-hours.* In the best
:l
l
urrent with the conduction of water
ill correspond to the quantity of w:
ours to the product of this quantit
[*compare* pp. 143, 144]

type of accumulator the former amounts to 90 to 96 per cent., and the latter only to 76 to 86 per cent. A small part of the loss of energy, amounting to from 14 to 24 per cent., is due to the transformation of a certain quantity of the energy of the current into heat during the process of charging, but the greater part of the loss is dependent on the fact that the opposing E.M.F., which has to be overcome by the charging current, amounts, on the average, to 2·2 volts whereas the mean E.M.F. of the charged accumulator is only 1·95 volts. The following example will make the meaning of these two quantities clearer. An accumulator is charged in eighteen hours with a current the average intensity of which is two ampères, and the average E.M.F. is 2·2 volts, and the accumulator is discharged in eight hours with a current of 4·25 ampères mean intensity and 1·97 volts average E.M.F. The quantity of current obtained, expressed in ampère-hours, is

$$\frac{4{\cdot}25 \times 8}{2 \times 18} \times 100 = 94{\cdot}4 \text{ per cent.}$$

And the energy of the current, expressed in watt-hours, is

$$\frac{1{\cdot}97 \times 4{\cdot}25 \times 8}{2{\cdot}2 \times 2 \times 18} \times 100 = 84{\cdot}5 \text{ per cent.}$$

The not inconsiderable loss of energy, from 15 to 25 per cent., is caused, to a small extent by the Joule-heat, but for the most part by the opposing force to be overcome by the E.M.F., which amounts to about 2·2 volts, while the accumulator produces, on an average, an E.M.F. of 1·95 volts while it is being discharged. The accumulator behaves like a reservoir of water, which is filled, and then sunk to a lower level. Considering this difference, amounting to ·2 to ·3 volt, one might suppose that the chemical processes in an accumulator are not completely reversible. Nevertheless, L. Dolezalek

ektrochemie, **4**, p. 349 [1898]) has proved the
he equation

$$2\,H_2SO_4 + PbO_2 \rightleftarrows PbSO_4 + 2\,H_2O + PbSO_4.$$

ging, ← charging), and has explained the differ-
M.F. Assuming the equation given above, he
d, thermodynamically, the relations between the
f an accumulator and the concentration of the
acid used therein, and demonstrated the agreement
the theoretical and empirical values. The following
ken from his memoir, shows that the E.M.F. of the
ulator decreases with decreasing concentration of
id.

TABLE XXII.

E.M.F.	Sp. Gr. of Sulphuric Acid.	Percentage of H_2SO_4.
2·29	1·496	58·37
2·18	1·415	50·73
2·05	1·279	35·82
1·94	1·140	19·07
1·82	1·028	3·91

w, the specific gravity of the acid in the porous masses
electrodes must increase on charging, and decrease on
re quickly than in the electrolyte; because
y diffusion cannot complete itself sufficiently
completion will be hindered the more, the
ent-intensity. Hence, while the accumulator
nd discharged, it behaves as if it contained
, and less concentrated, acid, respectiv
it to saying that the opposition-forc
r than the E.M.F. on discharging.

ore
way
ure
from
The
far the
an ac-
Let a
eaden plate
7 centims.
road, and 0·9 centim.
ded by platinum foil.
from the lead, and let
be immersed in dilute
eaden
latinum
several
wire
screws
to be
ic acid
ometer

f (bore=1·3 mm.), and the little rod *V*. Minute
of hydrogen at once begin to rise from the slips of
The liquid in the manometer rises about three
. per ten minutes. The volume of gas collected in a
eter tube amounts to about 2·5 c.c. in three hours.*
ough a certain loss of energy is unavoidable in using
ılators, nevertheless these elements possess many ad-
es over all other galvanic sources of current. To put
tly, these advantages consist in the high E.M.F., the
nternal resistance (only a few hundredths of an ohm),
ıe relatively large capacity and great constancy, of
:cumulator.

ıose who wish to become more fully acquainted with the essential
:s of accumulators are referred to the pamphlet, by Dr. Karl Elbs,
:kumulatoren [Leipzig : Barth ; 1893. 1 mark] ; also to E. Hoppe's
kkumulatoren für Elektricität [Berlin : Springer ; 1898].

CHAPTER IX.

THE ENERGETICS OF GALVANIC ELEMENTS.

ELECTRICAL energy possesses the great advantage that it can be stored easily, and can be changed into other forms of energy with but small loss.

Just as the mechanical work which a body falling freely is able to perform is measured by the product of the impelling force, which is conditioned by the height of the fall, into the mass of the body, so electrical energy is measured by the product of the difference of potential, π, into the quantity of current, i; that is to say, electrical energy is measured in volt-coulombs. And

1 volt × 1 coulomb = 10^7 ergs = 0·2362 calories = 10,185 gram-centims.

When a galvanic element with the E.M.F. π, and the internal resistance w_1, is closed by a conducting wire the resistance of which is w_2, the whole of the electrical energy, $\pi \times i$, is changed into heat; and if the current circulates for t seconds with a constant E.M.F., this heat is expressed by the statement

$$C = 0{\cdot}2362\ \pi \,.\, i \,.\, t = 0{\cdot}2362\ i^2\ (w_1 + w_2)\ t \text{ cals.}$$

The quantity of heat

$$c_1 = 0{\cdot}2362\ i^2 \,.\, w_1 \,.\, t \text{ cals.}$$

remains in the galvanic element; and the quantity of heat

$$c_2 = 0{\cdot}2362\ i^2 \,.\, w_2 \,.\, t \text{ cals.}$$

is developed in the connecting wire.

th these quantities of heat, c_1 and c_2, may be demonstrated rimentally, at any rate approximately, in a short time. aniell element with a porous cell is not very suitable as ource of the current, because a sufficiently powerful nt is not obtained from this arrangement by reason of latively large internal resistance. Neither can a Bunsen's nt—composed of zinc, chromic acid, and carbon—be yed, because the two electrodes produce heat directly electrolyte, and so heat is set free before the circuit is l. These drawbacks are not so apparent if accumulators ployed. A Böse's accumulator, of the Y type, is suitable; tains three plates 3·5 × 9 centims. in size, and possesses acity of two ampère-hours when a current of one ampère en from it. The double thermoscope of Looser* is s the heat-indicator. This consists (*see* figure 65) of the neters M_1 and M_2 and the two equal-sized receivers R_2, which are connected with the manometers by the houc tubes g_1 and g_2. Each receiver is constructed, principle of Bunsen's ice-calorimeter, of two cylindrical set one inside the other, and having their upper rims together. The inner vessel, which is to contain the nce to be heated, must be 4 centims. wide and 10 s. high, while the outer vessel has a diameter of 10 s. The heat produced in the first vessel presses out that is in the jacketing space between the two vessels, t the liquid rises in the limb of the manometer which ened on the scale S. [In an actual experiment] the ulator was placed in the receiver R_1 along with 95 c.c. ric acid (1 : 4). The receiver R_2 contained an equal y of sulphuric acid; and this receiver was close which carried two copper wires connected

btainable from Müller & Meiswinkel, in Essen, for 45 m

platinum wire, p, 25 centims. long and 0·1 mm. thick, and having a resistance of 2·5 ohms. When charged, the accumulator showed an E.M.F. of 1·9 volts, and an internal resistance of 0·15 ohm. When the liquids in the receivers had attained the temperature of the room

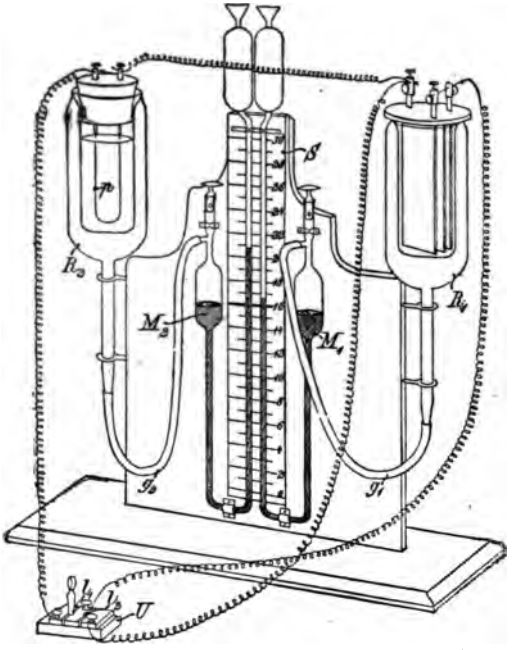


Fig. 65.

the wire for closing the circuit was adjusted in the way shown in figure 65 (the key of the switch U was placed in l_1). Under these conditions the quantity of current amounted to

$$i = \frac{1{\cdot}9}{0{\cdot}15 + 2{\cdot}5} = 0{\cdot}717 \text{ ampère.}$$

twenty minutes the quantity of heat which should be loped in R_1 was

$$c_1 = 0{\cdot}2362 \times {\cdot}717^2 \times {\cdot}15 \times 1200 = 21{\cdot}86 \text{ cals.};$$

in R_2 the quantity was

$$c_2 = 0{\cdot}2362 \times {\cdot}717^2 \times 2{\cdot}5 \times 1200 = 364{\cdot}28 \text{ cals.}$$

iat is to say, the quantities of heat should have been iated as $w_1 : w_2$, that is, as 1 : 16·6. As a matter of fact, ie threads of liquid in the manometers rose through 4 mm. nd 48 mm. respectively. Considering that heat was lost rom the conducting wire, and taking into account the other, ind not inconsiderable, deficiencies inherent in the process, he result was tolerably satisfactory.

When π is constant the ratio $c_2 : c_1$ increases if w_2 increases. But the absolute value of c_2 must diminish with an increment of w_2, because i decreases. In the case that π and t do not change, the value of c_2 reaches a maximum, namely,

$$c_2 = 0{\cdot}2362 \times i^2 \times w_2 \times t = 0{\cdot}2362 \left(\frac{\pi}{w_1 + w_2}\right)^2 \times w_2 \cdot t \text{ cals.}$$

$_2 = w_1$; and the heat in the element is equal to the heat the connecting wire, as is shown by experiment. The ids in the manometers rise to equal heights, namely, ı two minutes, provided that the platinum wire p er R_2 is replaced by another wire 3 centims. long, k, and having a resistance of 0·15 ohm. The ust certainly indicate a greater rise when π t. Because a claim is made on the accumu- onsiderably beyond its working power on sets in, and the E.M.F. falls ma yet greater degree if the accum putting the key of the switch

4. Nevertheless it is shown that almost the whole of the chemical energy of the element is changed into heat, for after short-circuiting for one minute, the liquid in the manometer M_1 has risen through 20 mm.

Moreover, the galvanic current is capable of performing work of a specific kind in apparatuses included in the circuit: the work may be mechanical, such as driving an electromotor which raises a weight; or it may be chemical, such as electrolysing a conductor of the second class, and separating therefrom constituents which, taken together, possess a greater energy-content than the compound. *In such cases the total heat of the current must be smaller, by the energy-equivalent of such work.* This also may be illustrated by experiment. A cork is placed in the receiver R_2; this cork carries a manometer fitted with a three-way cock, and two wires attached to pieces of platinum foil 1 sq. centim. area, in the manner indicated in the cell Z in figure 50 (p. 175). If these electrodes are kept 1·5 centims. apart, the resistance of the cell is 2·5 ohms, and hence as great as that of the platinum wire p in figure 65. The E.M.F. of the accumulator suffices to decompose the sulphuric acid in the receiver R_2. After a minute, the liquid in the manometer of R_2 (the bore of the tube of which is 2 mm.) shows a difference of level of 30 centims. Putting the sum of the kathodic and anodic polarisation as 1·7 volts, the quantity of electricity which flows per second through the cross-section of the path of the current is

$$\frac{1{\cdot}9 - 1{\cdot}7}{0{\cdot}15 + 2{\cdot}5} = {\cdot}0755 \text{ coulomb};$$

and hence, if no chemical work is done in the receiver R_2, the total heat of the current, after twenty minutes, will be

$$C = 0{\cdot}2362 \times 0{\cdot}0755 \times 1{\cdot}9 \times 1200 = 40{\cdot}66 \text{ cals.}$$

But as 1 coulomb evolves 0·00009351 gram of explosive gas

H+O], and as 68,400 cals. are required for the decomsition of 18 grams of water, the deficiency in the heat of : current brought about by the chemical work is

$$c = \frac{68400}{18} \times 0{\cdot}00009351 \times 0{\cdot}0755 \times 1200 = 32{\cdot}19 \text{ cals.}$$

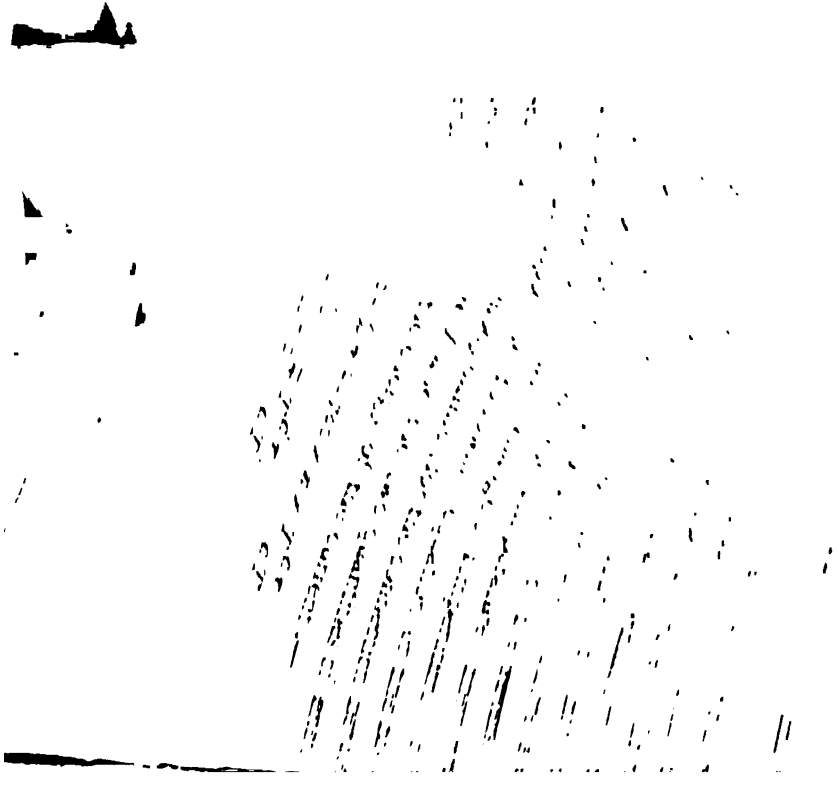
nce only $40{\cdot}66 - 32{\cdot}19 = 8{\cdot}47$ cals. are set free in the :uit. As a matter of fact, scarcely any change is to be n in the manometers M_1 and M_2.

f the platinum anode had been covered with copper ore the experiment began, and the current had been sent ough copper sulphate solution, instead of dilute sulphuric l, the quantities of heat, $c_1 = 21{\cdot}86$ and $c_2 = 364{\cdot}28$, it have been set free in the receivers R_1 and R_2, as nical work would not have been done.

here is another question which concerns the relations veen the electrical energy of a galvanic cell and the nical energy from which the former takes its origin. cell falls off in chemical energy the more the longer it uces an electric current, and the more lively are the nical changes in the cell, that is, the greater is the nal equivalent (expressed in calories) of the processes occur. It was supposed for a long time that, in accordwith Thomson's rule, the electrical energy which could ained corresponded exactly to the loss of chemical ther words, that the chemical heat was equal t heat developed in the total circuit of the ed that the current was not required to cial work. Now if π expresses the E.M.F. electrical energy per gram-atom of t it dissolves at the anode is

$$6{,}500 \times {\cdot}2362 = n \times \pi \times 22{,}782 \text{ cals.}$$

ne total thermal value of the ch



ı $d\pi/dT$ here denotes the temperature-coefficient
ıat is, the change of E.M.F. by a rise of 1°
.e ; it is obtained from measurements of the
:d π_2, of a cell at temperatures t_1 and t_2, by the

$$\frac{d\pi}{dT} = \frac{\pi_2 - \pi_1}{t_2 - t_1}.$$

t 22,782 $\times n \times T \times d\pi/dT$ is called the secondary
t is equal to the difference between the current-
π × 22,782 cals., and the chemical heat Q. If
negative, that is, if the E.M.F. decreases with
; temperature, then the electrical energy which is
e is less than the loss of chemical energy due to
nical changes in the element. In this case the
y heat is set free, besides the chemical heat Q, when
t is taken from the cell. On the other hand, if $d\pi/dT$
ve, that is, if the E.M.F. increases with increasing
ture, the element gives a greater current-energy than
'alent to the consumption of chemical energy, and
st be taken up from the surroundings, and converted
:ctrical energy, in order to keep the element at a
t temperature

ıccuracy of Helmholtz's equation has been completely
by Jahn and other investigators. A satisfactory
ent was found between the observed temperature-
ınd those calculated from the values of π and Q
'termined by experiment.

examples will more fully elucidate Helmholtz's
ıe cell

$$Pb/Pb(NO_3)_2/Ag_2(NO_3)_2/Ag_2$$

lues were found for every 206·4 grams
)°:—

Current-heat = 42,872 cals.
Chemical heat = 50,900 „

Hence the secondary heat is

$$22{,}782 \times 2 \times 273 \times d\pi/dT = -8028 \text{ cals.}$$

It follows that $d\pi/dT = -0{\cdot}000646$ volt; almost the same number was observed, namely $-0{\cdot}000632$ volt. Only 84 per cent. of the chemical energy was changed into electrical energy in this cell. The cell behaves like a steam-engine in which only a fraction of the heat set free by burning the coal is obtained as mechanical work.

The cell $Pb/Pb(C_2H_3O_2)_2/Cu(C_2H_3O_2)_2/Cu$ exemplifies the case of a positive temperature-coefficient. In this cell Jahn found

21,684 cals. for the current-heat, and
17,533 „ for the chemical heat.

The value, calculated from the secondary heat, which is +4151 cals., for $d\pi/dT$ is + 0·00334 volt, and the observed value was + 0·000385 volt. The fifth part of the energy of the current is derived from heat outside the cell. The cell transforms into electrical energy, not only the chemical energy of the processes that take place within it, but also a considerable quantity of heat from its surroundings, and in this respect it behaves like a volume of a gas which does work in expanding at the cost of the heat of its surroundings.

By far the greater number of galvanic elements have negative temperature-coefficients. Nevertheless the elements with positive temperature-coefficients are more interesting, inasmuch as they represent methods which change a certain amount of external heat into electrical energy. A cell of this kind, which is very suitable for purposes of demonstration, is described in a memoir by Bugarszki (*Zeit. für anorgan. Chemie*, **14**, p. 145). The apparatus shown in figure 37 (p. 150) is used. Pure mercury is poured over the bottoms of the beakers B_1 and B_2; the beakers are filled with normal solution

nitrate, which is intended to act as an indifferent
and the electrodes *a* and *k* are immersed in
The caoutchouc covers, wherein the electrodes
l, are provided each with an opening 8 mm. wide.
atus is connected with a small galvanometer, and
:d in a water-bath. If some compressed mercurous
ınd a few crystals of potassium chloride, are shaken
:he galvanometer is not affected. But immediately a
:k of potassium hydroxide is placed in B_1, the needle
› the 12th division, provided the temperature of the
ath is 16°. The electrode *a* is found to be the anode,
to be the kathode. If the water-bath is heated,
flection of the needle increases; at 55°, it reaches
wentieth division. If the cell is cooled, the needle
s backwards. A brown film of mercurous oxide appears
e mercury in B_1. The chemical changes in this cell,
KOH/KNO_3/HgCl/Hg, proceed according to the equation

$$2\,KOH + 2\,HgCl = Hg_2O + H_2O + 2\,KCl.$$

ıe causes of the current are as follows: the mercury ions
curous chloride are discharged at the electrode *a*;
:e chlorine ions attract the potassium ions of the
ıitrate, and the NO_3 ions attract the potassium
potassium hydroxide; and the OH ions of the
'e c use the mercury in B_1 to send ions into
2 IgOH gives $Hg_2O + H_2O$.
ıents show that the E.M.F. of the cell
846 volt at 43°·3. Hence

$$-\frac{\cdot 1483}{\cdot 3} = +\cdot 000838 \text{ volt.}$$

T. at 0° and 43°·3, are put into
›btains

$$+ 2 \times 22{,}782 \times 273 \times \cdot 000838,$$

$$+ 2 \times 22{,}782 \times 316\cdot 3 \times \cdot 000838.$$

Hence, $Q = -3586$, and -3401 cals. respectively. These values agree very well on the whole, considering the sources of possible error. The thermal value of the chemical processes is -3040 cals. (calculated from the data in Ostwald's *Lehrbuch der allgemeinen Chemie*); hence the results may be taken as confirmatory of the equation of Helmholtz, as the differences of 546 and 361 cals., respectively, are of no consequence in thermo-chemical statements. The behaviour of this cell is very noteworthy, inasmuch as it shows that an endothermic process can occur spontaneously by the abstraction of the necessary heat from outside.

Galvanic elements for which the rule of Thomson holds good must have a very small temperature-coefficient, that is to say, their E.M.F. is only very slightly influenced by the temperature. This holds not only for the element $Zn/ZnSO_4/CuSO_4/Cu$, but also for the calomel element $Zn/ZnCl_2/Hg_2Cl_2/Hg_2$, which is a very suitable normal element* (E.M.F. is almost exactly one volt), the temperature-coefficients of which have been determined to be $+ 0{\cdot}000034$ and $+ 0{\cdot}00001$, volt respectively.

The E.M.F. of a reversible cell can be calculated, by Helmholtz's equation, from the thermal value of the reaction which occurs, only when the temperature-coefficient is also known. As there is no doubt of the accuracy of that equation, it is possible to check the theory of the chemical processes which occur in a cell, by comparing the calculated and the empirical values of the E.M.F. of the cell. For the hydrogen-oxygen cell, $d\pi/dT = -{\cdot}00144$ volt; hence, at 18°,

$$\pi = \frac{34{,}180}{22{,}782} - 290 \times {\cdot}00144 = 1{\cdot}081 \text{ volts.}$$

* The Clark element, which is most commonly employed as a normal element, $Zn/ZnSO_4/Hg_2SO_4/Hg_2$, has an E.M.F. at 15° of 1·4336 volts; and its temperature-coefficient amounts to $-0{\cdot}00117$ volt.

π is 1·08 volts. Hence the current of
y the combination of the two gases to

teresting to carry out the calculation for
treintz has determined the temperature-
cells to be 0·00032 volt, and Tschelzoff
t of formation of lead peroxide [PbO, O] to
The thermal value of the processes occurring
kathode of an accumulator, referred to one
ad, is found in the following way :—

ode.

$O_4 + H_2O = H_2SO_4 + O \quad = -68{,}400$ cals.
$Pb + O = PbO \quad = +50{,}300$ „
$+ H_2SO_4Aq = PbSO_4 + H_2O = +23{,}400$ „

Sum = + 5,300 cals.

kathode.

$bO + H_2O = +50{,}300 + 68{,}400 - (50{,}300 + 12{,}140)$
$= +56{,}260$ cals.
$q = PbSO_4 + H_2O \quad = +23{,}400$ „

Sum = + 79,660 cals.

mal value of the reactions is therefore

$$Q = 5{,}300 + 79{,}660 = 84{,}960 \text{ cals.}$$

iven, at 15°,

$$\frac{84{,}960}{2 \times 22{,}782} + 288 \times 0{\cdot}00032 = 1{\cdot}957 \text{ volts.}$$

l value agrees so well with the observed value
ent affords the best confirmation of the theory
l changes in accumulators, developed in the
ter, according to which the lead plate and the
late are changed to lead sulphate when
lischarged. The equation is therefore sat

$$H_2SO_4 + PbO_2 \rightleftarrows PbSO_4 + 2H_2O + PbSO_4.$$

current passes from antimony to bismuth, the liquid in manometer rises about 40 mm. in a few minutes, which shows that the point of junction, *l*, has become heated. The current is now reversed, the liquid in the manometer falls 20 to 30 mm. below its original level, in consequence of the cooling of *l*; and when the current is stopped the liquid gradually rises to its original level, because of the withdrawal of heat by the point of junction from its surroundings.

The Peltier's effect is clearly observable when a current passes between a conductor of the first class and an electrolyte, but it is small at the surface of separation of two electrolytes. Jahn has measured the Peltier's effect at the points of contact of metals and solutions of their salts. It follows from his data that *the secondary heat of a galvanic element agrees with the algebraic sum of the Peltier's effects that occur at the electrodes.* Hence the secondary heat and the Peltier's effect are probably identical; a conclusion which also follows from the fact that *the secondary heat changes its sign when a current passes into the galvanic element in the reverse direction.* The secondary heats must be important in electrolytic processes. If the anode is soluble, the two heats neutralise each other at the electrodes; but if the anode is insoluble, the sum of the two heats are different. The laborious work of Jahn (*Zeit. für physik. Chemie*, **26**, p. 385 [1898], *see* pp. 185 to 193), has led to rich results which are found to be so important in determining decomposition-tension. Jahn found the values 1·570 and 1·494 volt for the dissociation, or decomposition-strain, $\mathfrak{P}$, at 0° C., of a solution of copper sulphate containing 1 gram molecular weight of the anhydrous salt in 10 litres; the temperature-co-efficient is

$$\frac{\mathfrak{P}_{10} - \mathfrak{P}_0}{20} = - \cdot 0038 \text{ volt.}$$

TABLE XXIII.

1	2	3	4	5	6	7	8
Electrolyte.	$\mathfrak{P}_0$	$\mathfrak{P}_{20}$	$\frac{d\mathfrak{P}}{dt}$	Electrical energy used $C_t = 2 \times 22{,}782\ \mathfrak{P}_t$ cals. at 0°	at 20°	Heat of formation Q cals.	$\frac{Q}{2 \times 22{,}782}$ volts
$ZnSO_4$	2·62	2·55	−·0035	119,380	116,190	106,090	2·33
$CdSO_4$	2·33	2·25	−·0038	106,160	102,520	89,880	1·97
$Pb(NO_3)_2$	2·03	1·96	−·0035	92,495	89,260	68,070	1·49
$CuSO_4$	1·57	1·49	−·0038	71,536	67,890	55,960	1·23
$Cu(NO_3)_2$	1·56	1·49	−·0035	71,080	67,890	52,410	1·15
$Ag_2(NO_3)_2$	1·10	1·04	−·0028	50,120	47,387	16,780	0·37

The thermal equivalent of the electrical work which is used in separating one gram-atom of copper, with an insoluble anode, at 0° and 20°, is

$$C_0 = 2 \times 22{,}782 \times \mathfrak{P}_0 = 71{,}536 \text{ cals.}$$

and

$$C_{20} = 2 \times 22{,}782 \times \mathfrak{P}_{20} = 67{,}890 \text{ cals.}$$

As the heat of formation, Q, of copper sulphate (Cu, O, SO_3 aq) is only 55,960 cals., only this quantity can be gained as chemical energy; hence, the rest of the energy will be set free in the form of heat in the decomposition-cell, namely, at 0° $q_0 = 16{,}570$, and at 20° $q_{20} = 11{,}930$ cals. The quantity of energy thus set free as heat at any temperature $t°$ is expressed by the general equation

$$q_t = \left[2 \times 22{,}782 \times \left(\mathfrak{P}_0 - t\frac{d\mathfrak{P}}{dt}\right) - Q\right] \text{cals.}$$

This secondary heat is localised at the electrodes in the form of Peltier-heat. According to Jahn's determinations, $q_a = -10{,}070$ cals will disappear at the copper kathode, and $q_a = 11{,}930 - (-10{,}070) = +22{,}000$ cals. will be evolved at the platinum anode, when $2 \times 96{,}540$ coulombs flow from

TABLE XXIII.

10	11	12	13	14	15
heats] cals. at 20°	Peltier-heats at 20°. Cals. q_k	q_a	Saving for 1°. Cals.	Temperature whereat $C_t=Q$	Quantities of metals separated, in grams.
10,100	− 10,170	+20,270	159	83·5°	65·0
12,640	− 8,770	+21,410	182	89·5°	112·0
21,190	− 2,340	+23,620	162	150·8°	207·0
11,930	− 10,070	+22,000	180	91·0°	63·7
15,480	− 10,070	+25,550	160	116·6°	63·7
30,607	+ 2,350	+28,257	137	243·3°	216·0

sulphate to a copper kathode. The Joule-heat, which ɔe added to these heats, was neglected in Jahn's ments, because of the exceedingly small current-in- and the trifling resistance of the decomposition-cell. vident that the amount of electrical energy consumed decomposition of copper sulphate decreases as tempera- ncreases. The saving per degree of temperature is

$$C_0 - C_{20}/20 = 2 \times 22{,}782 \times \frac{d\,\text{▮}}{d\,t} = 180 \text{ cals.}$$

ll ctrical energy were changed into chemical ondary heat (q_t) becoming equal to zero, the strain would be only $Q/2 \times 22{,}728 = 1{\cdot}23$ volts.

$$2\,\text{▮}\left(\text{▮}_0 - t\frac{d\,\text{▮}}{d\,t}\right) - Q = 0$$

um value would suffice for the he temperature 91°.

a series of data, taken from Jah lations of the electrical en is of certain salts of heavy hich can be obtained.

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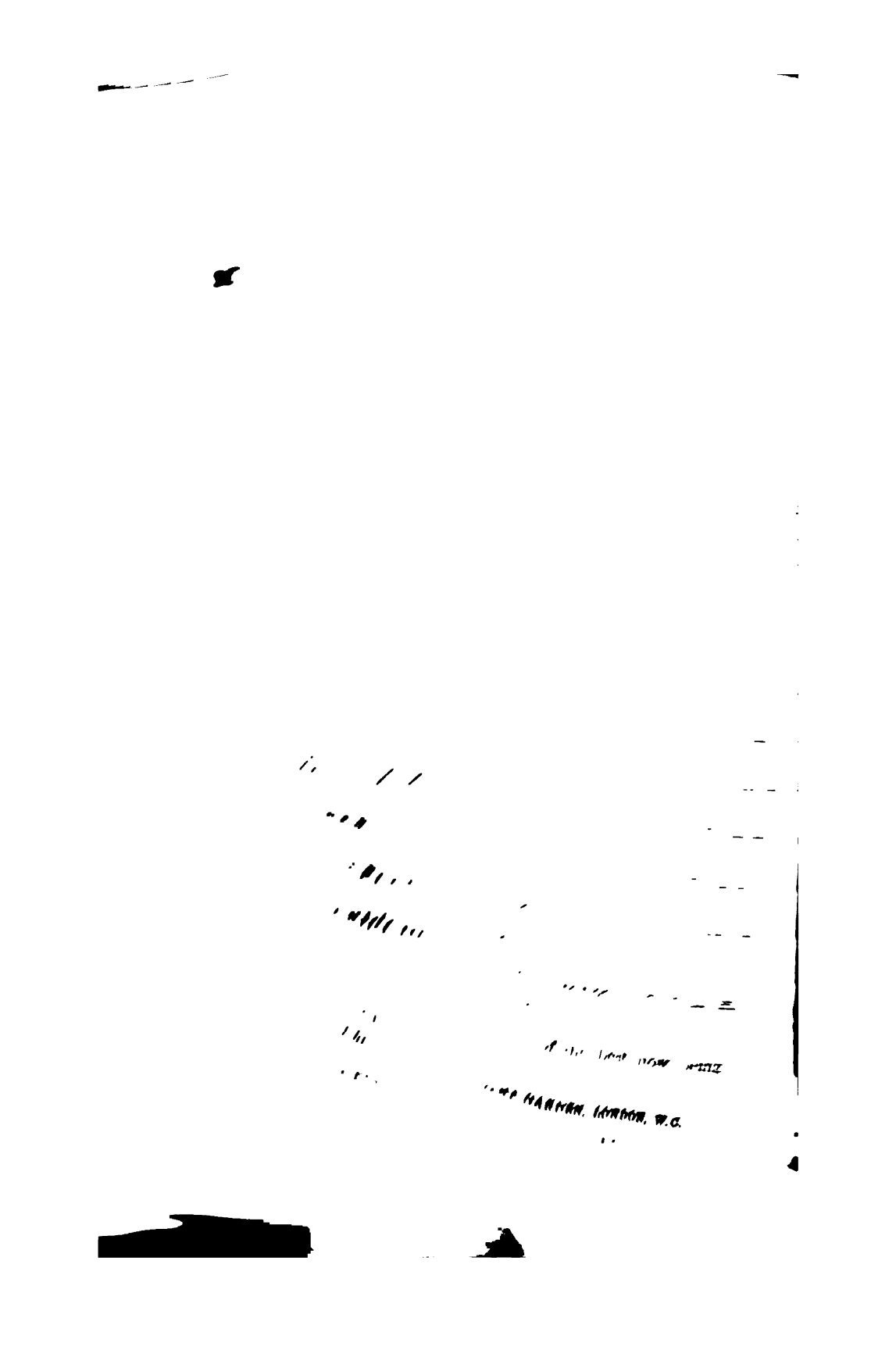

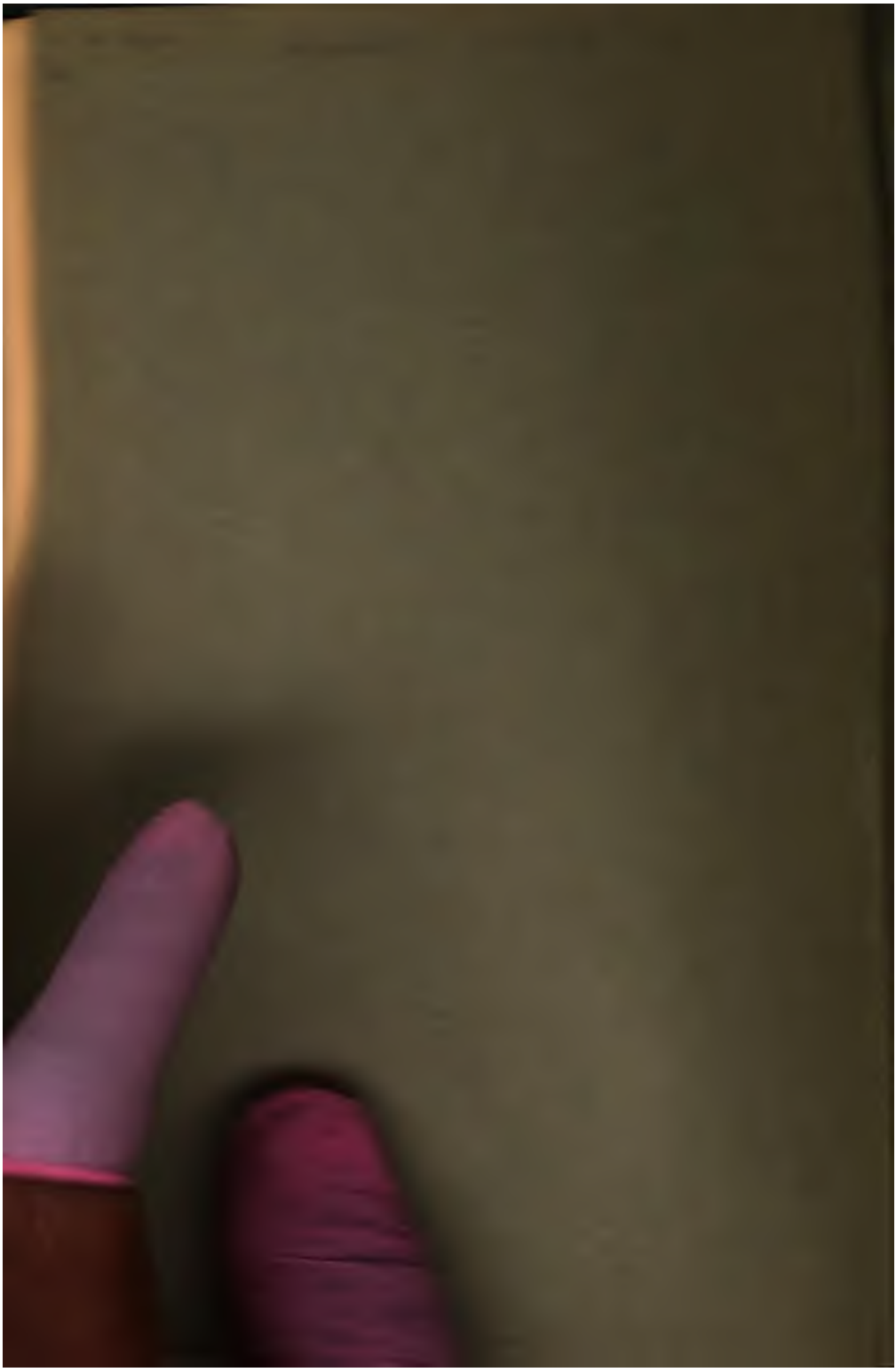

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